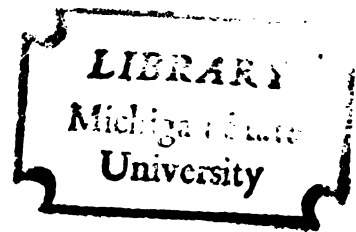


SPECTROSCOPIC STUDIES OF
THE ENVIRONMENT OF EXCHANGE
CATIONS IN SMECTITES

Dissertation for the Degree of Ph. D.
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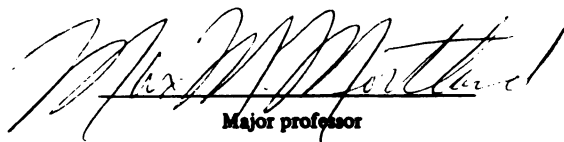


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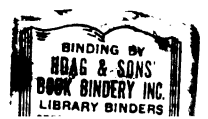
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ABSTRACT

SPECTROSCOPIC STUDIES OF THE ENVIRONMENT OF EXCHANGE CATIONS IN SMECTITES

By

Murray Brian McBride

The behavior of interlayer cations in smectites has been studied by electron spin resonance (esr) and infrared spectroscopy. The Cu^{2+} and Mn^{2+} ions tumble rapidly as hexaaquo complexes in the fully hydrated interlayers, but move into the hexagonal cavities of the silicate surface upon thermal dehydration. Limited layer charge reduction by these small divalent cations can occur as the dehydrated cations migrate further into vacant octahedral sites of dioctahedral minerals. While charge reduction is irreversible, cations move out of hexagonal holes as the interlayers are expanded during resolution of the clay. No evidence for specific adsorption of these cations on the silicate structure is observed.

Studies of line-broadening of the esr signal of interlayer Mn^{2+} indicate that Mn^{2+} - Mn^{2+} and Mn^{2+} - Fe^{3+} dipolar interactions are important. With increased hydration of the interlayers, the average distance between Mn^{2+} and structural Fe^{3+} increases, and the Mn^{2+} - Fe^{3+} interaction decreases. The interlamellar water in fully hydrated smectites has an apparent viscosity only 30% greater than water in solution. The $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ complexes of the interlayers become much less

mobile in air-dry smectites, and for clays heated to 200°C. the Mn^{2+} demonstrates an esr spectrum typical of crystalline matrices.

Studies of the esr of structural Fe^{3+} impurities in the octahedral layers of smectites have demonstrated the perturbation of structural Fe^{3+} by electrostatic interaction with exchange cations. This phenomenon allows the positions of cations in interlayers to be determined. Strongly solvating cations tend to tumble freely in fully expanded interlayers away from the silicate surface, while cations with low solvation energies remain near or within hexagonal cavities of the structure. A dielectric medium, such as water, in the interlayer reduces the electrostatic attraction between silicate and exchange cation, and the perturbation of structural Fe^{3+} is thereby decreased.

SPECTROSCOPIC STUDIES OF THE ENVIRONMENT
OF EXCHANGE CATIONS IN SMECTITES

By

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○ dehydrated clays
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INTRODUCTION

Recent interest in heavy metals as toxic pollutants of the environment has led to considerable research regarding the interaction of these metals with soils. Transition metals such as copper and manganese are stable in the soil environment as cations (e.g., Cu^{2+} - Mn^{2+}), and as such are able to occupy exchange sites of the clay minerals in the soil. Therefore, the nature of these adsorbed cations must be studied in order to determine the degree of toxicity and availability of clay-bound heavy metals. Such studies are difficult by chemical methods, but spectroscopic techniques allow the clay to be examined undisturbed. Electron spin resonance (esr) spectroscopy may be used to detect exchangeable Mn^{2+} or Cu^{2+} on clay surfaces at very low concentrations because of the paramagnetic properties of these ions. Similar investigations of natural soils are possible, but organic matter strongly chelates many transition metal cations. The present study uses only pure natural smectites; thus, the competing effect of metal chelation by organic matter is not present.

Cation positions in clay interlayers are known to be related to the hydration energy of the cation and the hydration conditions of the environment. Although most methods do not allow clay samples saturated with solvent to be studied directly (e.g., infrared spectroscopy), esr does not have this limitation. Thus, fully hydrated clays may be analyzed in addition to dry clays to determine the nature and

position of interlayer transition metal cations as well as the properties of interlamellar water. Paramagnetic exchange ions in the smectite interlayers may reflect their environment through changes in the esr spectrum. Similarly, paramagnetic iron of the clay structure may be affected by conditions at the silicate surface. In effect, these ions act as chemical "sensors" or "probes" to give information about their immediate surroundings.

PART I

Cu(II) INTERACTIONS WITH MONTMORILLONITE:
EVIDENCE FROM PHYSICAL METHODS

Introduction

Considerable research has been devoted to the study of adsorption and exchange properties of copper ions in soils and pure clay minerals. Although several workers have indicated that specific adsorption of Cu(II) ions on clay takes place (i.e., DeMumbrum and Jackson, 1956a and b), others have concluded that copper retention is similar to that of other divalent ions, suggesting error in interpretation due to the precipitation of $\text{Cu}(\text{OH})_2$ (Bingham et al., 1964). More recent work in infrared (Calvet and Prost, 1971) and electron spin resonance (ESR) spectroscopy (Clementz et al., 1973) has revealed the strength of physical methods in determining the nature and position of interlamellar cations. For example, exchangeable copper on smectite is strongly hydrated as the $\text{Cu}(\text{H}_2\text{O})_6^{++}$ ion in suspension, but upon air-drying, loses ligand water to form the interlamellar $\text{Cu}(\text{H}_2\text{O})_4^{++}$ species. Its hydrated nature is important in considering the feasibility of specific adsorption mechanisms that have been proposed.

In this study, Cu(II)-montmorillonites were heated in order to determine the changes associated with dehydration of the copper ions on the clay surface. Although Li(I) ion movement into the vacant octahedral positions of dioctahedral clays upon heating is a well-known phenomenon, divalent cation migration into the clay structure has not been closely studied. Farmer and Russell (1967) reported that 400°C heat treatment of Mg(II)-montmorillonite reduced the cation exchange

capacity (CEC) by one third. Calvet and Prost (1971) concluded from infrared studies that Ni(II) and Be(II) ions are able to occupy octahedral sites as well, while Ca^{++} and K^+ , because of their size, cannot penetrate the silicate layer. It was expected from these previous studies that Cu(II), because of its small ionic radius, could enter the octahedral positions.

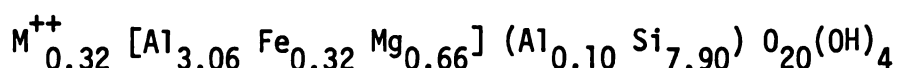
Electron spin resonance spectroscopy has been used to assess the hydration state and stereochemical orientation of copper ions on montmorillonite surfaces (Clementz et al., 1973; Clementz et al., in press) and could, therefore, be applied to these heated clays. Also, the changes in the "OH deformation" region of the infrared spectrum of heated montmorillonites allow interpretations to be made regarding the position of the interlamellar cations. Calvet and Prost (1971) described the effect of Li(I) movement into octahedral sites on the $600\text{-}950\text{ cm}^{-1}$ infrared region. Farmer and Russell (1964) have shown that perturbation of these bands can result simply from the dehydration of the interlayer cations, even when no ions penetrate to the octahedral positions.

The actual extent of migration of cations into octahedral positions (i.e., the degree of CEC reduction) has been difficult to measure because layer charge reduction produces non-expanding clays which contain some cations in the "hexagonal holes" formed by oxygen atoms on the surface of the 2:1 structure. Brindley and Ertem (1971) found that a few solvents, including ethanol, would expand these reduced-charge clays. Thus, in this study, ethanol was used to expand heated montmorillonite and solvate ions positioned in the hexagonal holes of

the lattice and make them available for exchange, thus permitting an accurate measurement of the actual loss in layer charge upon heating.

Methods and Materials

The Cu(II)-saturated montmorillonite was prepared by separation of the $< 2\mu$ clay fraction of an Upton, Wyoming bentonite having the chemical formula:



(Ross and Mortland, 1966). It was washed in $CuCl_2$ solution five times and the suspension was then dialyzed with distilled water until the suspension supernatant gave a negative $AgNO_3$ test for chloride. The CEC of the clay was determined to be 89.3 meq. Cu(II) per 100 grams by conductometric titration with NaOH, and 86.9 meq. Cu(II) per 100 grams by repeated exchange with $1M CaCl_2$ solution at pH 4 and analysis by atomic absorption. This establishes the validity of the conductometric method as well as the divalent nature of the exchangeable copper ion.

Heat treatments were done, in an oven controlled to $\pm 1^\circ C$, on self-supporting films dried from the clay suspension. These films, placed on glass slides, were X-rayed on a Norelco diffractometer using filtered Cu-radiation. Infrared spectra of the films were obtained on the Beckman IR-7 spectrophotometer.

The CEC values of the montmorillonite were determined by suspending the samples in 1:1 H_2O -95% ethanol and titrating this suspension conductometrically with 0.01 N NaOH to determine the amount of exchangeable copper. Heat treatment for CEC analysis involved placing

the freeze-dried clay samples in an oven at various temperatures for twenty-four hours.

Electron spin resonance spectroscopy of the oriented clay films was done in quartz tubes using a Varian E4 spectrometer. Orientation studies on these films were accomplished by the method of Clementz et al. (1973). Magnetic susceptibility measurements were done on about 1.0 gram samples of freeze-dried clay by the Gouy method.

Results and Discussion

X-ray diffraction and CEC data.--While an air-dry Cu(II)-montmorillonite film has a $12.4\text{\AA}$ basal spacing, representing a monolayer of $\text{Cu}(\text{H}_2\text{O})_4^{+2}$ ions (Clementz et al., 1973), the collapsed spacings observed for clays heated to 156°C and above indicate loss of ligand water (Table 1). This does not imply that the ion is totally dehydrated; thermogravimetric studies of the Cu(II)-montmorillonite (unpublished data) indicate that 1-2 water molecules per Cu(II) ion are present at 200°C . Such a monohydrate (or dihydrate) form is likely very similar to that proposed by Farmer and Russell (1964) for Mg(II)-vermiculite, with both the Cu(II) ion and its associated water molecule(s) positioned in hexagonal holes of the silicate layer.

Ethanol expanded the basal spacings of all montmorillonite samples to $17.0\text{--}17.3\text{\AA}$ regardless of the temperature of heat treatment (Table 1). Brindley and Ertem (1971) had similar observations for reduced charge Li(I)-montmorillonites that were unable to swell in water. However, these Cu(II)-clays were able to slowly expand in water after heating to $150\text{--}200^\circ\text{C}$, but failed to re-expand after the 270°C

heat treatment. Although both 200°C heated Cu(II) and Li(I)-montmorillonites swell to 17 Å in ethanol, subsequent washing of these clays in water results in collapse of the Li(I)-clay to 9.9 Å while the Cu(II)-clay expands further to 21.5 Å. The apparent difference between the two heated clays is that the Li(I) form loses enough charge to become non-expandable in water, while the Cu(II) form must retain enough charge to remain expandable. The greater the hydration energy of the exchange cation, the lower is the critical layer charge still permitting swelling in water (Brindley and Ertem, 1971). An interesting observation from Table 1 is that 1:1 water-95% ethanol swells the clay more as the temperature of heat treatment is increased. From Table 2, no change in CEC is observed until 156°C, while CEC reduction is essentially complete at 200°C. Thus, the loss of layer charge explains the increasing expandability of the clays in 1:1 water-95% ethanol as temperature of heating increases. Brindley and Ertem (1971) found similar evidence for increased swelling of clays in ethanol and other solvents as the charge density was lowered. The 1:1 water-95% ethanol solvent expands the layers further than 95% ethanol alone (Table 1). The higher dielectric constant of water gives it greater capabilities than ethanol in swelling clays to high basal spacings; however, ethanol is much more effective than water in allowing montmorillonite layers, totally collapsed by heat, to re-expand at all. The 270°C heated Cu(II)-clay gives evidence for this, remaining collapsed in water despite having considerable layer charge (57.0 meq. per 100 grams), yet swelling in both 95% ethanol and 1:1 water-95% ethanol. As Brindley and Ertem have concluded, water and ethanol appear to have completely different mechanisms of layer swelling.

Table 1. X-ray 001 spacings of Cu(II)-montmorillonites after 24-hour heat treatment and equilibration in several solvents for two weeks.

Solvent used	Heat treatment (C°)					
	None	50°	100°	156°	200°	270°
air-dry	12.4	12.0	11.7	9.7	9.7	9.3
H ₂ O	19.4	19.4	19.6	(9.8) 14.2*	(9.9) 15.2*	9.7 (9.6)
1:1 water-95% ethanol	21.5	22.0	22.1	23.2* (23.9*)	26.7* (26.0*)	26.7* (9.7)
95% ethanol	17.3	17.3	17.0	17.0	17.0	17.0*

* very interstratified

Parentheses indicate basal spacings observed immediately upon addition of solvent.

Table 2. CEC values for Cu(II) montmorillonite heated to various temperatures for 24 hours.

Solvent of Titration	Heat treatment (C°)					
	None	50°	100°	156°	200°	270°
water	83.7	80.7	84.8	61.9	38.9	17.0
1:1 water- 95% ethanol	89.3	82.5	89.8	68.2	59.6	57.0

The CEC data (Table 2) show a correlation of layer charge reduction to the collapsed basal spacings (air-dry) of Table 1. Titration in 1:1 water-95% ethanol is considered to give actual layer charge measurements, while titration of the clay in water results in CEC data which depend on the quantity of layers which can be re-expanded after heating. As Table 1 indicates, increased temperatures of heating caused more and more clay layers to be non-expanding in water, until the 270°C treatment resulted in a CEC corresponding to only external surface Cu(II). The value of 17.0 meq. per 100 grams is very near the expected CEC of external sites of smectite. As with Li(I)-montmorillonites, the loss of layer charge is interpreted as being a result of Cu(II) migration into vacant sites of the octahedral clay. Unlike the Li(I)-clays, charge loss is only about 1/3 of the total CEC, even at 270°C. A second heat treatment of a reduced-charge Cu(II)-montmorillonite (58.0 meq. Cu(II) per 100 grams) was done at 200°C after resaturation of remaining exchange sites with Cu(II) using three washes in 1:1 95% ethanol-1.0M CuCl₂ solution. The resulting CEC from NaOH titration of the clay suspended in 1:1 water-95% ethanol was 58.3 meq. Cu(II) per 100 grams, indicating that the initial reduction in charge is a maximum. Greater Coulombic repulsion forces for the divalent copper ion than for the monovalent lithium ion in the silicate lattice may account for the reduced entry of Cu(II) into octahedral sites. Movement into these sites requires considerable dehydration of the Cu(II) ions so that they may first enter the hexagonal cavities of the lattice, as shown by the 9.3-9.7 Å basal spacings of the reduced charge clays. The almost totally dehydrated Cu(II) ion positioned in a hexagonal hole of the

silicate is the transition state for migration into the octahedral vacancy of the dioctahedral mineral (Calvet and Prost, 1971), at which time complete dehydration must occur. For cations with no direct access to vacant octahedral sites, the "transition state" is a metastable position as long as the clay is prevented from rehydrating.

Infrared Spectroscopy

Significant perturbations of the infrared OH deformation region for Cu(II)-montmorillonite after heating to 200°C are apparent (Figure 1. a,b). The 848 cm^{-1} band, assigned to OH associated with AlMg pairs (Calvet and Prost, 1971), is lost upon heating and seems to be shifted to a frequency higher than the 855 cm^{-1} band observed by Calvet and Prost upon heating a Li(I)-montmorillonite. It appears as a shoulder on the low frequency side of the 889 cm^{-1} , assigned to OH associated with AlFe pairs (Farmer and Russell, 1967). However, re-expanding the heated clay in 1:1 water-95% ethanol or titrating the clay with NaOH in 1:1 water-95% ethanol give identical spectra (Figure 1. c, d). A shoulder around $850\text{--}860\text{ cm}^{-1}$ appears, while the shoulder on the 889 cm^{-1} band is lost, indicating a significant shift of the AlMgOH band to lower frequency. Both of the above treatments swell the layers, allowing resolution of only the Cu(II) ions that are present in hexagonal hole positions, thus causing the ions to move out of these sites. The titration with NaOH after swelling the layers produces $\text{Cu}(\text{OH})_2$, assuring the removal by precipitation of all Cu(II) ions from the hexagonal sites. Thus, the effect of removal of Cu(II) ions from the lattice hexagonal holes is to reduce the perturbation of the OH associated with

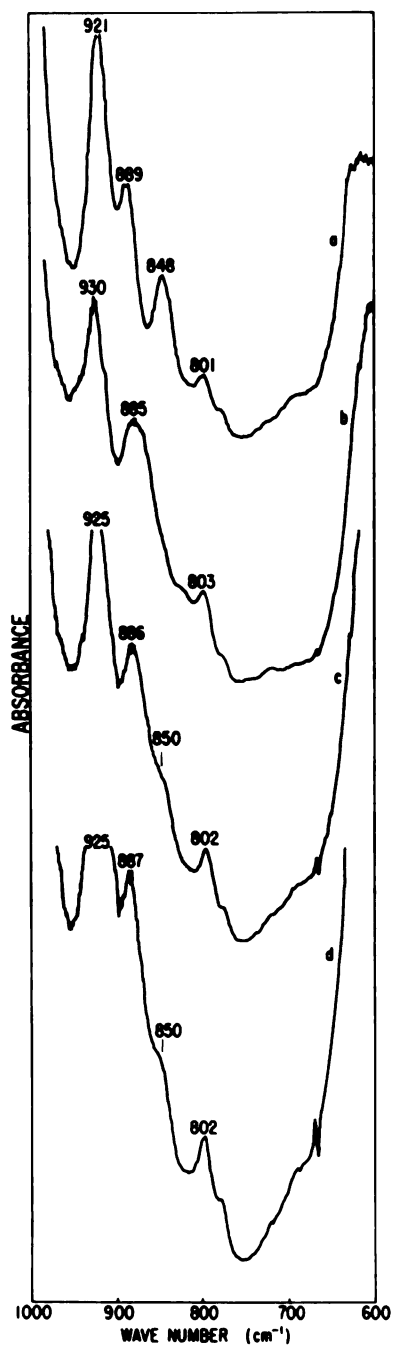


Figure 1. Cu(II)-montmorillonite, infrared OH deformation region:

- a. air-dry
- b. after 24 hour 200°C heat treatment
- c. after 24 hour solvation of b in 1:1 water-95% ethanol
- d. after NaOH titration of b

AlMg pairs. This is expected, since Cu(II) ions embedded in hexagonal hole positions would be situated directly above structural OH groups, and could change the direction of the dipole moment of the OH group as well as perturb its deformation vibration. Movement of Cu(II) into vacant octahedral sites must account for the remaining shift of the AlMgOH group from 849 to 850-860 cm^{-1} after the other Cu(II) ions have been removed from hexagonal cavities, since the spectrum of the unheated Cu(II)-montmorillonite cannot be regained by the solvation and titration techniques mentioned above. This "octahedral shift" is very similar to that observed for Li(I) montmorillonite after heating (Calvet and Prost, 1971). The larger "hexagonal hole shift" was not observed for the Li(I)-clay, probably because a divalent ion in the hexagonal hole perturbs the OH deformation much more than a monovalent ion in the same position.

The AlFeOH band near 889 cm^{-1} and the MgMgOH band at 803 cm^{-1} (Calvet and Prost, 1971) are not affected by heating the Cu(II)-montmorillonite to 200°C. However, the AlAlOH band at 920 cm^{-1} is shifted to near 930 cm^{-1} upon heating, and shifts back to 925 cm^{-1} when the hexagonal hole Cu(II) ions are resoluted (Figure 1). The explanation for this observation is very similar to that for the AlMgOH band shift, but the effect on the AlAlOH groups by Cu(II) moving into vacancies associated with AlMgOH groups must be less direct.

From Figure 2, it is apparent that Cu(II) ion movement into hexagonal hole and octahedral positions of the silicate lattice does not occur until well above 100°C. This observation is confirmed by the CEC and X-ray data (Tables 1 and 2). The infrared spectrum of the OH deformation region, after being altered at 156°C, changes little from

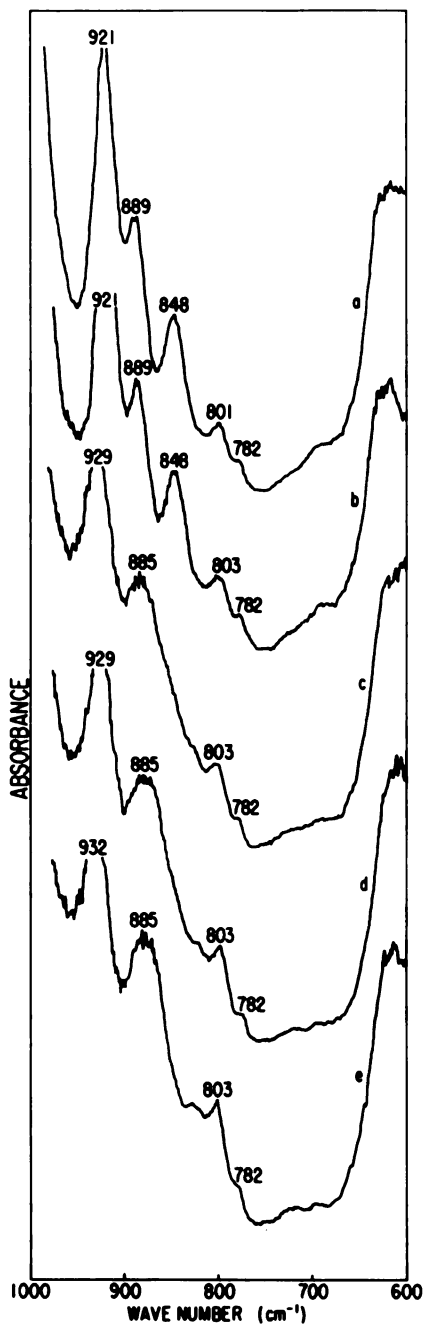


Figure 2. Cu(II)-montmorillonite, infrared OH deformation region:

- a. air-dry
- b. after heating 24 hours to 100°C
- c. after heating 24 hours to 156°C
- d. after heating 24 hours to 200°C
- e. after heating 24 hours to 270°C

156°C to 270°C, indicating that most of the Cu(II) migration has occurred at 156°C. The CEC data show that 2/3 of the maximum layer charge reduction took place at 156°C, while maximum reduction was reached at 200°C.

No change in the OH deformation region has been observed for Ca(II)-montmorillonites heated to 400°C (Calvet and Prost, 1971). However, from the above discussion it would be expected that Ca(II) ions, although too large to enter vacant octahedral sites, could occupy hexagonal holes and perturb the OH deformation vibrations in a manner similar to Cu(II) ions. This was observed (Figure 3), since heating Ca(II)-montmorillonite to 200°C caused the 847 cm^{-1} band to broaden and shift to 854 cm^{-1} . After a few minutes of exposure to air, the band returned to its original position, indicating that the Ca(II) ions were moving out of hexagonal cavities and rehydrating, thus removing the perturbation on the structural OH groups. The regeneration of the original OH deformation spectrum was nearly complete after 24 hours (Figure 3, c), indicating almost complete rehydration. In contrast, the reduced charge Cu(II)-montmorillonite does not rehydrate readily and Cu(II) ions remain in hexagonal holes, as indicated by the lack of change in the OH deformation region of a Cu(II)-montmorillonite exposed several days to air (40% relative humidity). This inability to rehydrate in the atmosphere is most likely related to the loss of layer charge.

Montmorillonite samples exchanged with various other cations were heated to 215°C for 24 hours, and the spectra were examined for irreversible changes in the OH deformation region after rehydration in

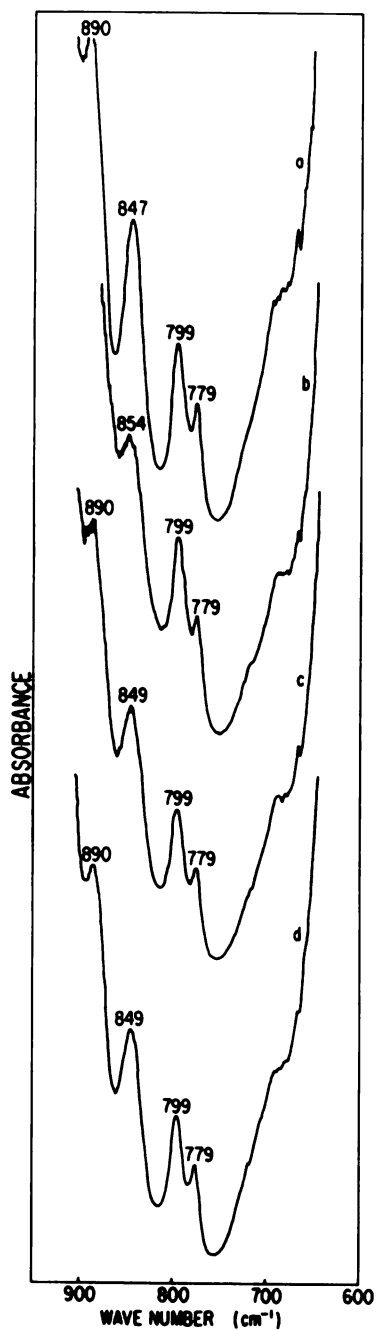


Figure 3. Ca(II)-montmorillonite, infrared OH deformation region:

- a. air-dry
- b. after 24 hour 200°C heat treatment, spectrum taken immediately after heating
- c. same as b, but spectrum taken after 15 minutes exposure to air (40% relative humidity)
- d. same as b, but spectrum taken after 24 hours exposure to air

air. All clays showed the marked shifts due to movement of dehydrated cations into hexagonal holes, but only the Cd(II) and Ca(II) clays showed regeneration of the 847 cm^{-1} band as rehydration in air took place. This indicates that Cd(II) cations (as well as Ca(II) as discussed before, and Na(I) and K(I) as determined by Calvet and Prost) cannot migrate into octahedral sites; the ionic radii of these ions are too large to permit penetration (Table 3). However, as Calvet and Prost (1971) have stated, movement into vacant octahedral sites is a general phenomenon of all small cations, as Table 3 indicates. Although the enthalpy of hydration of the cations must influence the temperature at which dehydration begins, and thus affects the temperature at which penetration of the structure begins, it is not a factor in determining whether or not migration to octahedral sites will occur. For example, Ca(II) and Cd(II), although having the lowest hydration enthalpies of all the divalent cations listed in Table 3, are not able to penetrate to the octahedral layer. While multivalent ions have the ability to penetrate the structure, charge seems to affect the extent of penetration as shown by the limited layer charge reduction by Cu(II) as compared to Li(I).

ESR Spectroscopy

The Cu(II)-montmorillonites, after heat treatment to various temperatures, were investigated in the air-dry state by electron spin resonance spectroscopy, using oriented films parallel and perpendicular to H_0 , the magnetic field. The orientation technique allows determination of the degree of anisotropy of the Cu(II) resonance (Clementz

Table 3. Ability of interlamellar cations to occupy octahedral sites of montmorillonite upon 215°C heat treatment for 24 hours.

Cation	Ionic radius (Å) [†]	Enthalpy of hydration [‡] (Kcal./mole)	Penetration of octahedral layer
Be ^{++*}	0.35	-596	+
Mg ⁺⁺	0.66	-459	+
Li ⁺	0.68	-124	+
Rh ⁺⁺⁺	0.68	Unknown	+
Ni ⁺⁺	0.69	-503	+
Cu ⁺⁺	0.72	-502	+
Co ⁺⁺	0.72	-477	+
Zn ⁺⁺	0.74	-489	+
Cd ⁺⁺	0.97	-432	-
Na ^{+*}	0.97	-97	-
Ca ⁺⁺	0.99	-377	-
K ^{+*}	1.33	-77	-

* From Calvet and Prost (1971)

† From Handbook of Chemistry and Physics

‡ From Cotton and Wilkinson, Advanced Inorganic Chemistry, 3rd edition

et al., 1973). Decreasing Cu(II) signal intensity is apparent with increasing temperature of heat treatment (Figure 4 a). However, regeneration of signal occurred upon re-swelling the films in 95% ethanol (Figure 4 b), indicating that Cu(II) ions in the hexagonal holes of the unexpanded clay either form bonds which cause the unpaired d-orbital electrons of Cu(II) to become paired, or the ions in the hexagonal environment experience relaxation effects which broaden the ESR signal to the point of being unobservable. The latter explanation is more probable for two reasons: (a) a covalent Cu(II) bond should not simply be broken by resolution of the Cu(II) ion by ethanol, unless it is very weak; (b) enhanced interaction of the Cu(II) ion with lattice vibration and paramagnetic Fe(III) ions of the structure can result when the ion is no longer hydrated and rapidly tumbling, but is positioned in the hexagonal holes of the lattice. This interaction causes a very short spin-lattice relaxation time which broadens the ESR signal greatly (Adrian, 1968). The 156°C heat treatment reduces signal intensity greatly, with little more reduction in intensity from 156° to 270°C, verifying the conclusion from infrared data that layer collapse and Cu(II) dehydration and movement into hexagonal holes first occurs (and is virtually complete) with the 156°C treatment. Part of the weak Cu(II) signal of the clays heated to 156°C-270°C and then equilibrated in air is isotropic with an electronic g factor of about 2.16 (Figure 4 a), and probably results from rehydration of external surface Cu(II) ions in the air, allowing the $\text{Cu}(\text{H}_2\text{O})_6^{++}$ species to form and tumble rapidly at the surface (Clementz et al., in press). The more narrow resonance near $g = 2.06$ is an anisotropic signal, showing little

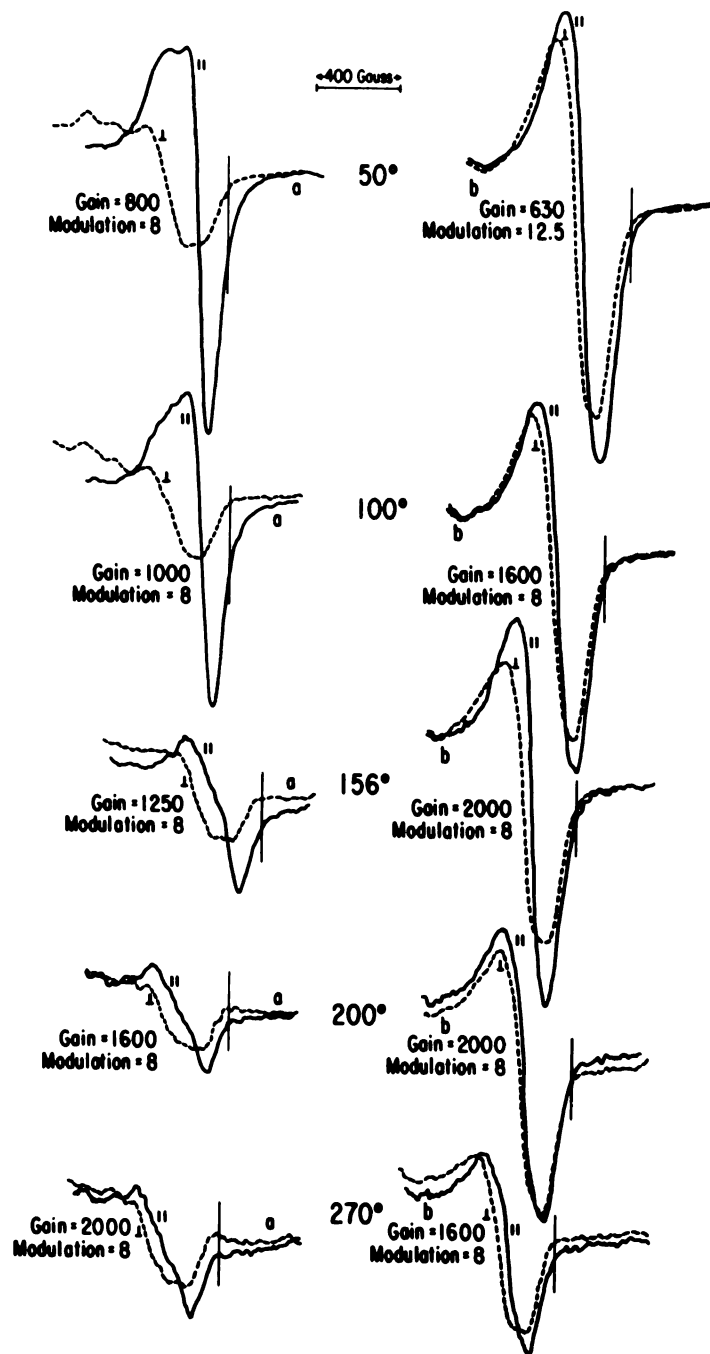


Figure 4. ESR spectra of Cu(II)-montmorillonite films heated to various temperatures for 24 hours:

- a. air-dry
- b. soaked in 95% ethanol several hours

The vertical lines represent the resonant position ($g = 2.0028$) of a standard strong pitch sample. The symbols || and ⊥ indicate the orientation of the ab plane of the silicate layers with respect to the magnetic field, H_0 .

intensity when the clay film is oriented perpendicular to the magnetic field, H_0 . Thus, 2.06 is the value for $g_{\perp}$ (Clementz et al., 1973), and the anisotropic signal represents Cu(II) in a restricted interlamellar environment. The $g_{\parallel}$ value for the anisotropic signal could not be accurately determined because of low signal intensity, but is known to be near 2.34 (Clementz et al., 1973). As the anisotropic spectra of the clays heated to 50°C and 100°C reveal, (Figure 4 a), Cu(II) is largely in a restricted environment of tetragonal symmetry after heating to these temperatures, the $\text{Cu}(\text{H}_2\text{O})_4^{++}$ species predominating in the inter-layer regions.

Resolution of Cu(II) ions by swelling the layers of heated clays in ethanol for several hours regenerates much of the ESR signal, as stated above. This signal, although quite isotropic for clays heated to low temperatures, shows more anisotropic character for those heated at higher temperatures. The isotropic signal at $g = 2.15$ indicates that the Cu(II) ions are solvated and tumbling rapidly between layers that are known from X-ray studies to be about $7.0\text{\AA}$ apart. The anisotropy at higher temperatures indicates that some layers did not totally expand upon addition of ethanol, thus preventing complete resolution of all Cu(II) ions. Some layers of the clays heated at high temperature must not have re-expanded at all, since signal intensity after ethanol treatment was reduced as temperature of heating increased.

If Cu(II)-montmorillonite is not exposed to air after 24 hours of heating at high temperature (215°C), almost no signal can be observed (Figure 5 a), indicating that almost completely dehydrated Cu(II) ions give almost no ESR signal (a weak anisotropic signal is present), nor

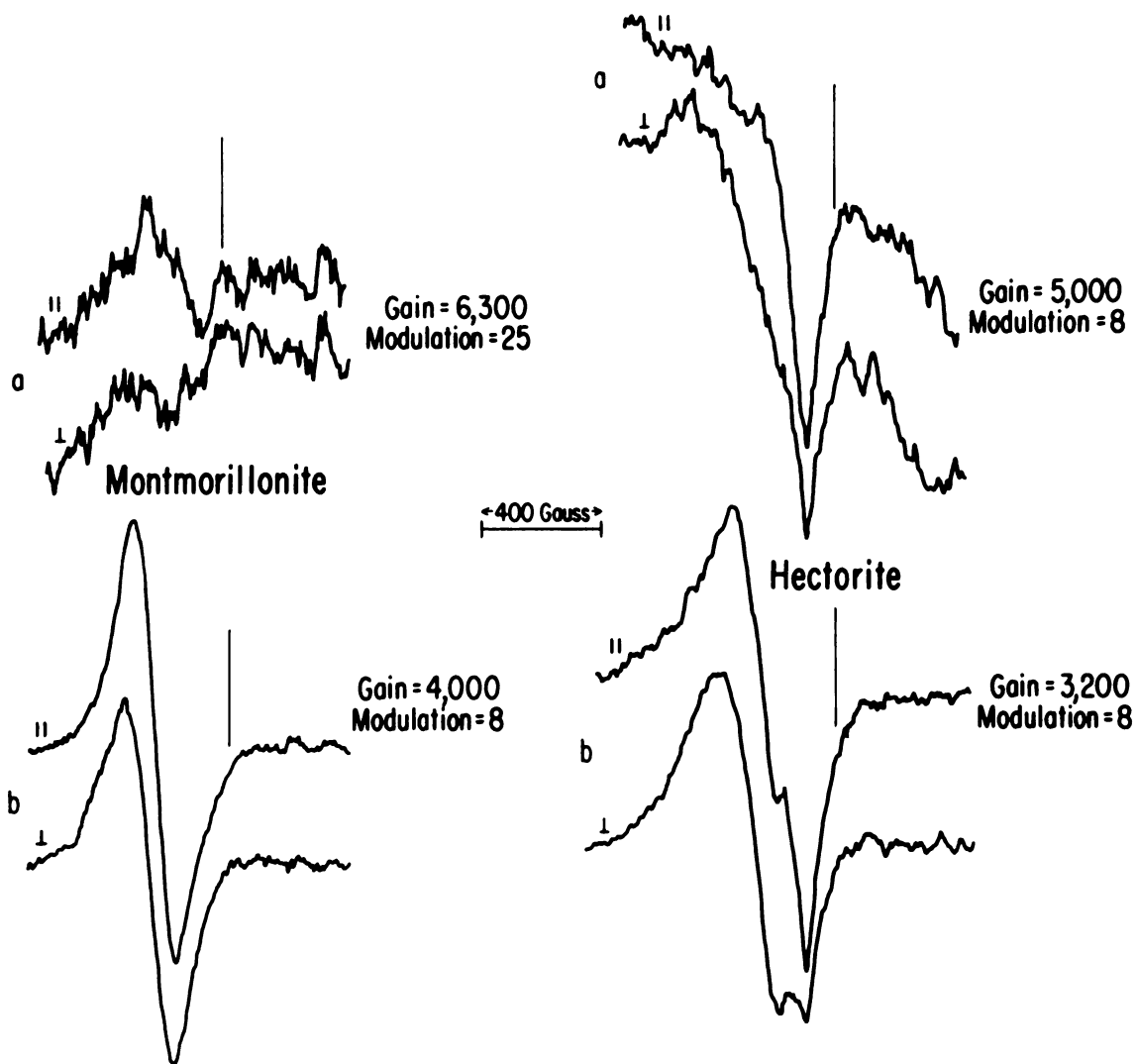


Figure 5. ESR spectra of Cu(II)-montmorillonite and Cu(II)-hectorite heated to 215°C for 24 hours:

- a. not exposed to moisture after heating
- b. exposed to a free water surface for 24 hours

do Cu(II) ions that enter octahedral sites of the structure. For both types of Cu(II), the loss of resonance can be explained by a too efficient spin-lattice relaxation, as described before. However, spin-pairing through a partially covalent Cu-O bond is a possible explanation for signal loss of Cu(II) which has migrated to vacant octahedral sites of the silicate lattice. Irrespective of the mechanism of signal loss, it can be stated that none of the ESR signals observed can have any appreciable intensity resulting from structural Cu(II). Thus, the isotropic resonance observed for air-dry films after heating to 156°C-270°C (Figure 4 a) must have resulted from rehydration of external surface Cu(II) as proposed above, since the X-ray diffraction data indicate that the clay heated to 270°C cannot re-expand in water to allow inter-layer cation rehydration. The weak anisotropic signal of the same films must have been due to restricted Cu(II) of the internal surfaces. In Figure 5, a similar anisotropic signal is observed for hectorite not exposed to air after heating to 215°C, again indicating that partially or totally dehydrated Cu(II) in hexagonal holes of the internal surface produce the signal. Penetration of Cu(II) into the octahedral layer is impossible in hectorite since it is trioctahedral. This resonance, hardly detectable for Cu(II)-montmorillonite if not exposed to the air after heating to the same temperature (Figure 5), may be reduced in intensity by the presence of Fe(III) in montmorillonite, hectorite containing very little Fe(III). Equilibration of both the heated hectorite and montmorillonite with a free water surface for 24 hours resulted in isotropic signals becoming fairly strong (Figure 5 b), indicating hydration of internal as well as external surface Cu(II) ions.

Magnetic Susceptibility Studies

As mentioned above, loss of ESR signal intensity may be a result of electron pairing (bonding) or relaxation processes. The former reduces the number of unpaired electron spins in a system while the latter does not. The magnetic susceptibility of a sample is a measurement of these unpaired spins and does not depend on spin-lattice relaxation processes. The magnetic moment of the electron interacts with an external magnetic field to change the apparent weight of the sample. Such susceptibility measurements were made on three freeze-dried montmorillonite samples: Cu(II)-saturated, Cu(II)-saturated and heated 24 hours at 200°C, and Ca(II)-saturated. For the Ca(II)-montmorillonite, the susceptibility was totally attributed to Fe(III), the only paramagnetic ion of appreciable quantity in the clay. The resulting effective magnetic moment, μ_{eff} , was 6.44 B.M. (Bohr magnetons), close to the value of 5.9 observed in many high-spin Fe(III) compounds (Figgis and Lewis, 1964). The theoretical magnetic moment for the high-spin Fe(III) ion ($S = 5/2$) is 5.92 B.M., and can be altered little by crystalline electric fields of a lattice, since its total orbital angular momentum is zero ($L = 0$) and there can be no spin-orbit coupling (J. Smart, 1966). Thus, Fe(III) in montmorillonite is in the high-spin state and its spin-only magnetic moment is not much changed by the silicate lattice. Paramagnetic impurities in the clay may account for the somewhat high value for Fe(III).

Still calculating susceptibilities on the basis of one mole of Fe(III) in montmorillonite, Cu(II)-clay had $\mu_{\text{eff}} = 6.27$ B.M., and

the same clay heated to 200°C for 24 hours had $\mu_{\text{eff}} = 6.61$ B.M. The Cu(II)-montmorillonite would be expected to have a susceptibility higher than the Ca(II)-clay, since Cu(II) in most compounds has $\mu_{\text{eff}} = 1.9$ B.M. The low value observed for the unheated Cu(II)-clay indicates that spin interaction between Cu(II) and Fe(III) may be occurring, a process of antiferromagnetism which is often observed in lattice structures (Figgis and Lewis, 1964). Superexchange, or spin exchange through intervening nonmagnetic atoms is the explanation for this phenomenon, and oxygen atoms are very effective in providing spin transfer, which would be necessary for superexchange to operate in silicates. Spin exchange between Cu(II) and Fe(III) may occur over several Angstrom units through structural oxygen atoms coordinated to these transition metals.

The fact that heated Cu(II)-montmorillonite has a magnetic susceptibility similar to the unheated Cu(II)-clay substantiates the conclusion that the loss of ESR signal of this clay upon heating must not be a result of Cu(II) spin pairing either by bonding to the silicate or by Cu-Cu interaction. The susceptibility for the heated Cu(II)-montmorillonite appears to be higher than that for the unheated Cu(II)-clay because of loss of hydration water upon heating.

General Discussion

Analysis of all the data presented indicates that Cu(II) ions remain hydrated on the clay interlamellar surfaces until enough thermal energy is provided to remove ligand water and permit migration into hexagonal holes of the lattice. Further movement through these sites

into empty octahedral positions of the montmorillonite occurs simultaneously but is limited, probably by the divalent charge on the ions. Ions considerably larger than Cu(II) cannot enter octahedral sites because of their size, and thus cannot reduce the layer charge.

The bond between Cu(II) and structural OH of clay proposed by DeMumbrum and Jackson (1956b) is not possible at ambient temperatures because the interlamellar $\text{Cu}(\text{H}_2\text{O})_4^{++}$ species of air-dry montmorillonite has a structure which would permit closest approach of Cu(II) and structural OH of more than $4\overset{\circ}{\text{A}}$. This distance is longer than any conceivable bond-length. Heating to about 150°C removes ligand water, permitting the dehydrated Cu(II) ions to approach structural OH by moving into hexagonal cavities. Still no evidence for bond formation is found, since resolution of the Cu(II) in hexagonal holes occurs upon layer expansion. The infrared evidence given by DeMumbrum and Jackson to support Cu-O bonding should be reconsidered for the following reasons: 1) mixing and compression of clay samples into KBr pellets allows ionic exchange with K(I) from the KBr to form K(I)-saturated clays (Mortland, unpublished data). Thus, the spectra reported would not be of Cu(II)-clay, but of K(I)-clay; 2) the bands at 6.4 and 7.0μ (1562 and 1428 cm^{-1}), attributed by DeMumbrum and Jackson (1956b) to Cu-oxygen bonds, are at a frequency too high for such vibrations, which usually are found in the far infrared region (i.e., $300\text{--}600\text{ cm}^{-1}$). An interesting observation is that these two bands coincide with the two most intense absorption bands for acetate anion, suggesting that if the clays were prepared with copper acetate, not all of the excess salt had been removed when the clay was saturated. This further suggests that

excess Cu(II) found above the exchange capacity might be due to Cu acetate; 3) the width of the OH stretch bands of their spectra indicate that most of the peak intensity is due to adsorbed and coordinated water (which varies with the nature of the exchangeable cation), so that measurement of the structural OH peak intensity under the conditions described is not a valid quantitative method.

Hodgson et al. (1964) have proposed endothermic chemisorption to explain "specific adsorption" of Co(II) on montmorillonite surfaces. However, the heat of reaction they calculate (about 15 kcal./mole) for Co(II) adsorption is not nearly sufficient to overcome the hydration energy of -477 kcal./mole for Co(II) and this exchange ion, like Cu(II), remains hydrated to high temperatures in the interlayer and on external surfaces. Thus, interaction of Co(II) with the lattice OH groups at the experimental temperatures that Hodgson et al. used is not likely for the same reasons given in the discussion on the feasibility of specific adsorption of Cu(II). The present study agrees with the findings of Bingham et al. (1964), that Cu(II) behaves much like other divalent ions on clays. A thermodynamic investigation of Cu(II)-Ca(II) exchange on montmorillonite (El-sayed et al., 1970) supports this view, indicating that Ca is somewhat preferred to Cu on the exchange sites even though the entropy term points to a more orderly structure of Cu ions on the surface. The latter observation implies structured hydration of Cu(II) ions on interlamellar surfaces as has been demonstrated by ESR (Clementz et al., 1973). This ordering would be expected to be greater for Cu(II) than Ca(II) for two reasons: (a) the Cu(II)-H₂O bond is partially covalent with d orbital-ligand orbital interaction; (b) the

coulombic ion-dipole interaction between cation and ligand is stronger for Cu(II) than Ca(II) because of the smaller copper ion radius.

The penetration of the octahedral layer by Cu(II) and other ions (Table 3) is not likely to be of importance in soils, but may be possible in the geologic column where the environment (temperature and pressure) might promote such interaction.

PART II

ELECTRON SPIN RELAXATION AND THE MOBILITY OF MANGANESE(II) EXCHANGE IONS IN SMECTITES

Introduction

The significant chemical and physical properties of smectites often depend on the nature of the interlayer exchange ions. To better elucidate the structure and mobility of the exchange ions, several workers have recently applied electron resonance spectroscopy to certain Cu^{2+} - and Mn^{2+} -saturated forms. Fully hydrated Cu^{2+} -montmorillonites, for example, have been shown to possess tetragonal $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ions which tumble rapidly in expanded interlayers containing several molecular layers of water (Clementz et al., 1973). Upon drying the mineral in air, the exchange ions lose two axial water ligands which are held weakly because of Jahn-Teller distortion of the d^9 electronic configuration of the metal ion. The resulting planar $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ions are confined to 2.8Å-thick interlayer regions with the symmetry axis of the complex ion oriented at 90° to the silicate lamellae.

Furuhata and Kuwata (1969) have reported that the widths of the hyperfine (hf) lines of hydrated Mn^{2+} are broader on the exchange sites of montmorillonite than in bulk solution. The increase in line width was attributed to relaxation effects of the more restricted surface-adsorbed ions. Also, Mn^{2+} -montmorillonite has been reported to exhibit broader hf lines when larger molecules (i.e., pyridine) replace water on ligand positions, a result again interpreted in terms of reduced mobility of the Mn^{2+} -solvent complex because of the size or bonding nature of the ligand molecules (Pafomov, et al., 1971;

Taracevich and Ovcharenko, 1972). However, in addition to mobility effects, other factors such as the site symmetry of the paramagnetic ion and dipolar interactions can also contribute to the observed esr line widths. The present study investigates the esr spectra of Mn^{2+} smectites of differing charge density and structural Fe^{3+} content under hydrated and anhydrous conditions. The relaxation mechanism controlling the hf widths of the mineral-bound ion has been defined, and a quantitative estimate of interlayer mobility has been obtained for fully hydrated hectorite.

Materials and Methods

The smectites used in this study are given in Table 1 along with their cation exchange capacities and reported unit cell formulas. The Mn^{2+} -saturated exchange forms were prepared by washing the native mineral (<2 μ fraction) with aqueous 1.0 M MnCl_2 . Excess salt was removed by dialysis with distilled water, and the mineral was recovered from the slurry by freeze-drying methods. Average Mn^{2+} - Mn^{2+} distances within an interlayer were estimated from the CEC values and the theoretical surface area of 800 m^2/g (Grim, 1968c).

X-ray basal spacing were determined with a Norelco diffractometer and Ni-filtered Cu-radiation. The magnetic susceptibilities of Mn^{2+} -hectorite, -montmorillonite, and -nontronite were measured by the Gouy method. The susceptibilities were corrected for paramagnetic contributions due to structural Fe^{3+} by subtracting the susceptibilities obtained for the Na^+ or Ca^{2+} exchange forms of the minerals. Only Na^+ -hectorite, which has a low Fe^{3+} content, showed no paramagnetism.

Table 1. Mn²⁺-saturated layer silicates.

	C.E.C., meq/100g	Unit Cell Formula	Reference
Vermiculite (Llano, Texas)	200	Mn _{1.00} [Al _{0.30} Fe _{0.02} Mg _{5.66}](Al _{2.28} Si _{5.72}) ₂₀ (OH) ₄	Foster, 1961
Montmorillonite (Chambers, Arizona)	116	Mn _{0.48} [Al _{2.84} Fe _{0.35} Mg _{0.85}](Al _{0.22} Si _{7.78}) ₂₀ (OH) ₄	Schultz, 1969
Nontronite (Garfield, Washington)	104	Mn _{0.42} [Al _{0.26} Fe _{3.70} Mg _{0.04}](Al _{1.00} Si _{7.00}) ₂₀ (OH) ₄	API, H-33A
Montmorillonite (Upton, Wyoming)	92	Mn _{0.32} [Al _{3.06} Fe _{0.32} Mg _{0.66}](Al _{0.10} Si _{7.90}) ₂₀ (OH) ₄	Ross and Mort- land, 1966
Hectorite (Hector, California)	73	Mn _{0.32} [Mg _{5.42} Li _{0.68} Al _{0.02}](Si _{8.00}) ₂₀ (F,OH) ₄	API, Project 49

X-band esr spectra were obtained with a Varian E-4 spectrometer. Oriented, self-supporting film samples, in which the crystallographic a and b axes of each clay platelet lie in the plane of the film, were prepared by previously described methods (Clementz et al., 1973). The average widths of the $m_I = \pm 5/2$ transitions (outer two resonance components) of the mineral-bound Mn^{2+} signals were estimated by measuring the peak to peak separation between the lines and subtracting the field separation of analogous lines for the ion in dilute solution. This method assumes that the hyperfine splitting A is the same in the mineral and in dilute solution. The validity of the assumption was verified by observing an A value of 90 ± 1 G for the 5% Mn^{2+} -doped Mg^{2+} hectorite, which is in agreement with the value of 95 ± 1 G reported for $MnCl_2$ in dilute solution (Levanon and Luz, 1968).

Results and Discussion

X-Ray Spacings

Since $Mn(H_2O)_6^{2+}$ is stable in aqueous solution, the ion is expected to be the major species present on the exchange sites of hydrated smectites. When two molecular layers of water are present in the interlayer, alignment of the octahedral faces of the ion with the silicate surfaces should give 001 basal spacings in the range 14-15 Å as is observed for $Mg(H_2O)_6^{2+}$ and $Cu(H_2O)_6^{2+}$ in vermiculite (Hougardy et al., 1970; Clementz et al., 1973) and for $Ca(H_2O)_6^{2+}$ (Brown, 1961) on montmorillonite. The observed spacings (Table 2) for the minerals under air dried conditions confirm the presence of the $Mn(H_2O)_6^{2+}$ ion.

Table 2. Basal spacings ($\text{\AA}$) of Mn^{2+} -saturated layer silicates.

	Air Dry Mineral	Fully Hydrated Mineral
Hectorite	15.0	22.0
Montmorillonite (Upton)	14.9	19.6
Nontronite	14.9	19.4
Montmorillonite (Chambers)	13.9*	19.2*
Vermiculite (Llano)	14.35 [†]	14.35 [†]

* Broad diffraction line, indicating interstratification.

[†] Very sharp diffraction peak.

With the exception of vermiculite, all of the Mn(II) clays expand at 100% relative humidity to give basal spacings of 19.2 - 22.0 Å. In general, the degree of interlayer expansion increases with decreasing silicate charge density. Thermal dehydration at 200° for 24 hours leads to migration of the Mn(II) ions to hexagonal cavities formed by the surface oxygen atoms or, in the case of the dioctahedral minerals, to vacant octahedral positions in the silicate structure (McBride and Mortland, 1974). Thus, the dehydrated minerals exhibit basal spacings (ca. 9.5 Å) typical of totally collapsed layers.

Magnetic Susceptibilities

The high spin ($S = 5/2$) configuration of octahedral Mn^{2+} is preferred to the low-spin state with almost all ligands, including water, so that a magnetic moment near 5.9 B.M. is expected. Based on the reported unit cell compositions of hectorite, montmorillonite and nontronite, susceptibilities corresponding to effective moments in the range 6.5 - 7.1 B.M. were obtained for the mineral-bound $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ ions under air-dried conditions. Deviations of the observed moments from the expected moment are attributed to uncertainties in the Gouy method and unit cell compositions. Within experimental error, however, no change in the susceptibility was observed upon dehydrating the minerals at 200°. Thus, no spin pairing or change in oxidation state of Mn^{2+} occurs upon thermal dehydration.

Esr Spectra

The esr spectrum of Mn^{2+} in solution normally consists of six hf lines due to coupling of the $S = 5/2$ electron spin with the $I = 5/2$

nuclear spin. Each hf component consists of three superimposed Lorentzian lines due to the five $\Delta m_s = 1$ transitions $|\pm 5/2\rangle \longleftrightarrow |\pm 3/2\rangle$, $|\pm 3/2\rangle \longleftrightarrow |\pm 1/2\rangle$, and $|-1/2\rangle \longleftrightarrow |+1/2\rangle$ which are not resolved at X band frequencies. The non-degeneracy of the $\Delta m_s = 1$ transitions leads to inhomogeneous line broadening. The line widths are the sum of two contributions, $\Delta H_i = \Delta H_{Ii} + \Delta H_{Di}$ where ΔH_I is the width arising from ion-solvent collisional relaxation processes (Rubinstein et al., 1971; Luckhurst and Pedulli, 1971) and ΔH_D is the width due to dipolar interactions between neighboring Mn^{2+} ions (Hinckley and Morgan, 1966). The ΔH_D term is concentration dependent, because the dipolar interactions are proportional to r^{-3} , where r is the average $Mn^{2+} - Mn^{2+}$ distance. In dilute solution (<0.01 M, $r > 55 \text{ \AA}$) the lines are narrow and determined exclusively by ΔH_I . Increasing the concentration causes the six hf components to broaden markedly until at concentrations of 2.3 M or greater ($r < 9.0 \text{ \AA}$) the hf structure is lost and the spectrum appears as a single broad line (Hinckley and Morgan, 1966).

A typical spectrum for $MnCl_2$ in dilute solution is shown in Figure 1 a. Fully hydrated Mn(II)-hectorite exhibits a similar "solution-like" spectrum, except that the hf lines are broader (Figure 1 b). Reducing the amount of interlayer water from several to two molecular layers by allowing the mineral to dry in air at ~50% relative humidity causes the lines to broaden markedly (Figure 1 c). Thermal dehydration at 200° for 24 hours leads to still further line broadening and almost complete loss of hf structure (Figure 1 d). Similar increases in line width with decreasing hydration are observed for the Mn^{2+} -saturated montmorillonites and nontronite.

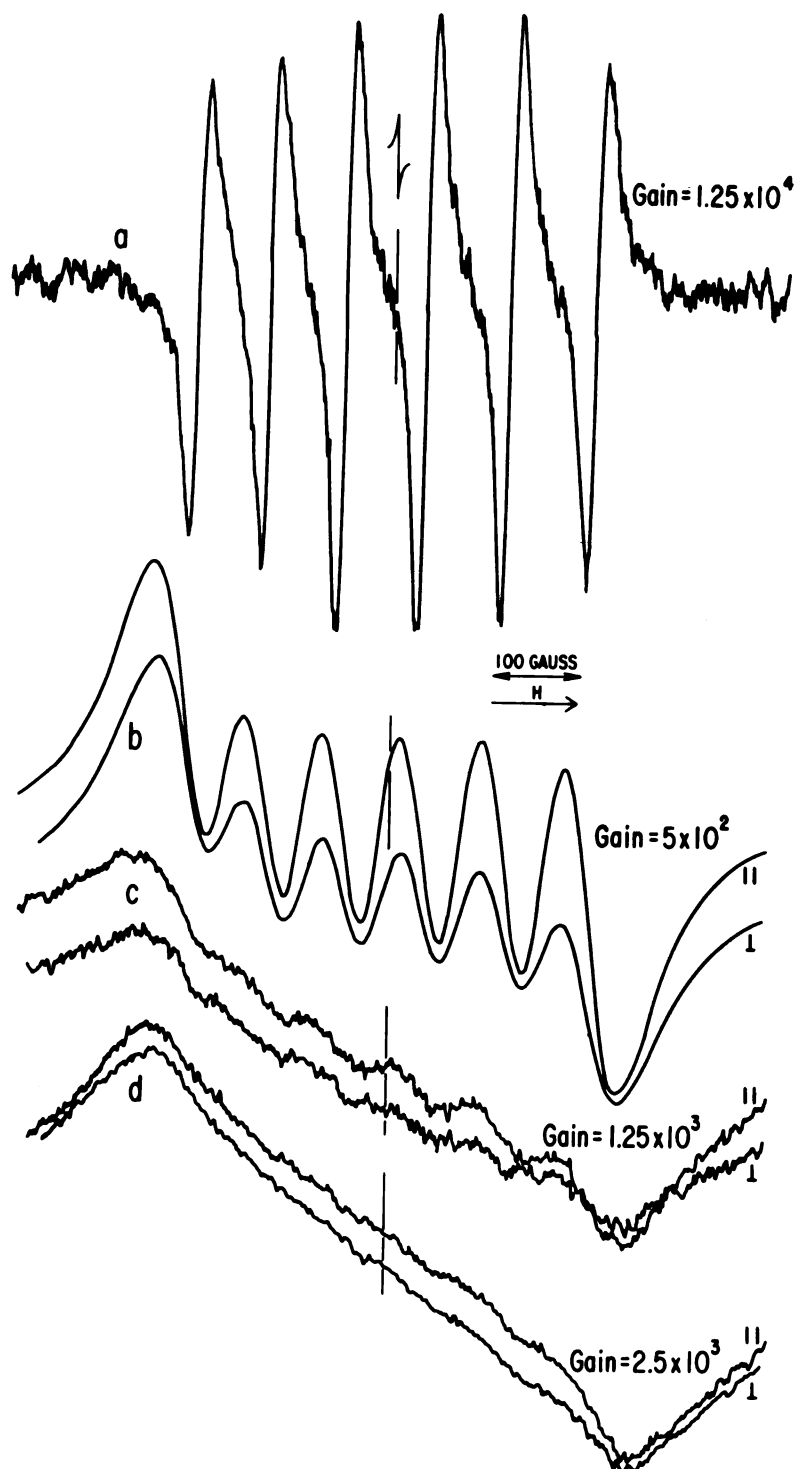


Figure 1. Room temperature esr spectra for a) MnCl_2 in methanol ($5.0 \times 10^{-5} \text{ M}$), and powder samples of hectorite; b) fully hydrated; c) air-dried; and d) dehydrated at 200°C for 24 hours. The vertical lines represent the resonance position of a standard pitch sample ($g = 2.0028$).

Since the average interlayer exchange ion distance for each mineral is in the range 10-14 Å, the widths of the Mn^{2+} signals should be determined mainly by the ΔH_D term. This is verified by the comparison in Figure 2 of the average width of the $m_I = \pm 5/2$ lines for MnCl_2 in methanol solutions and the fully hydrated minerals. Further evidence for the importance of dipolar broadening is provided by the spectrum of Mn^{2+} -vermiculite. The interlayer exchange ion distance in this latter mineral (6.9 Å) is substantially smaller than 9.0 Å, and, as expected, only a single, broad line with a width of 710 G is observed. The broadening is similar to that observed for the solid MnCl_2 salt (830 G) and consistent with dipole-dipole coupling between magnetic ions 3 to 8 Å apart (Abragam and Bleaney, 1970).

In addition to dipolar coupling between Mn^{2+} ions within an interlayer, analogous interactions between ions in adjacent interlayers may occur. Also, the Mn^{2+} ions may be relaxed by coupling to Fe^{3+} in the silicate structure. These dipolar interactions along the crystallographic $\underline{c}$ direction should differ from those in the $\underline{a}$ $\underline{b}$ plane and should be manifested as differences in line widths and g values when the magnetic field direction is oriented $\parallel$ and $\perp$ to the silicate sheets. Figure 3 illustrates the spectra obtained for an oriented film sample of air-dried Upton montmorillonite. The average width of the $m_I = \pm 5/2$ lines is 15 G larger for the $\parallel$ than for the $\perp$ orientation. The g values also differ slightly for the two orientations, 2.005 vs. 2.000 for the $\parallel$ and $\perp$ orientation, respectively.

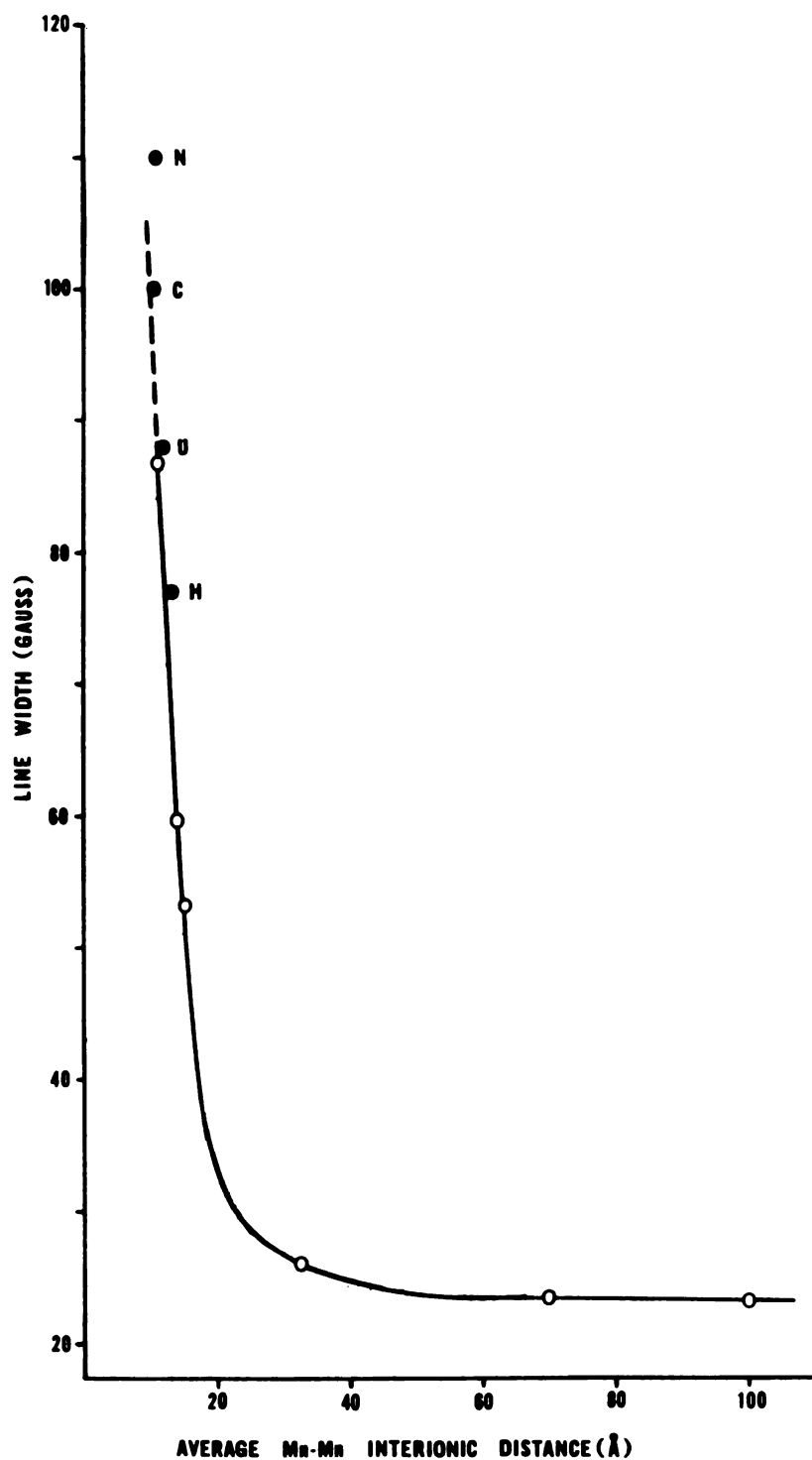


Figure 2. Dependence of the average $m_I = \pm 5/2$ line widths of Mn^{2+} on interionic distance. Open points are for MnCl_2 in methanol solution, solid points are for nontronite (N), Upton (U) and Chambers (C) montmorillonites, and hectorite (H) under fully hydrated conditions.

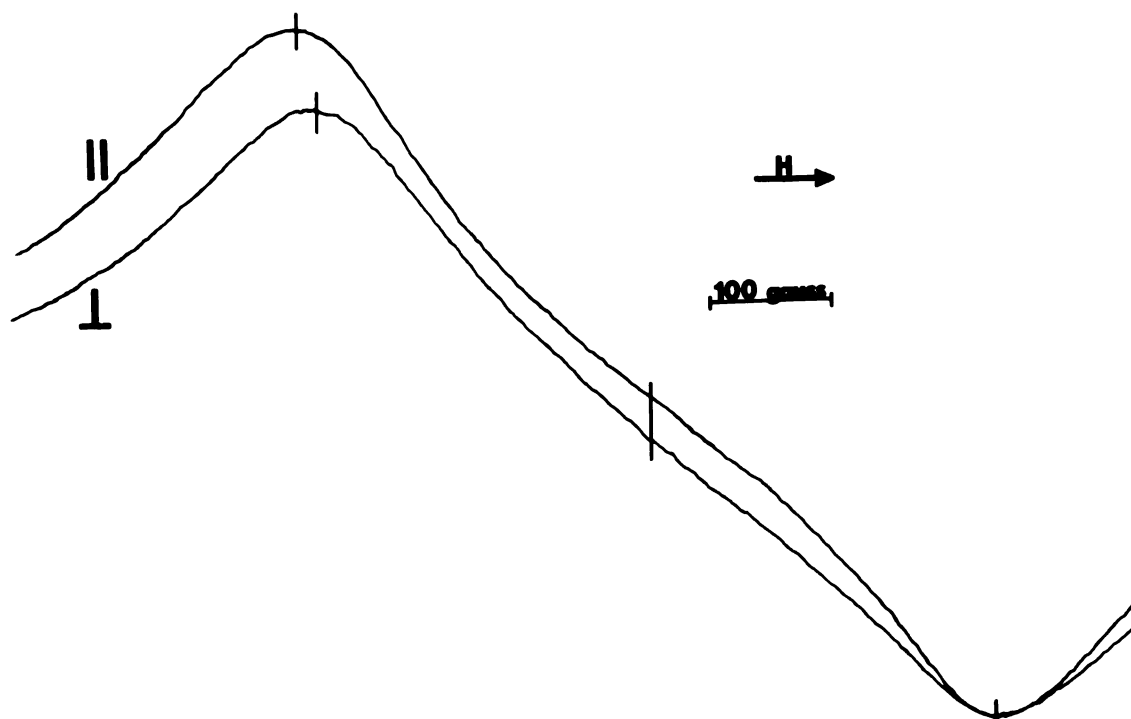


Figure 3. ESR spectra for an oriented film sample of air-dry Upton montmorillonite with the magnetic field direction || and ⊥ to the plane of the silicate sheets.

Table 3 summarizes the widths for oriented samples of each mineral under air-dried and fully hydrated conditions. With the exception of hectorite, the widths for the air-dried samples differ by ca. 15 G for the two orientations, whereas the widths are more nearly equal for the fully hydrated samples. The dependence of the magnetic anisotropy on hydration state is not unexpected. In the air-dried minerals, the motion of the $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ ions is confined to the a b plane, but in the fully hydrated state the ions may tumble more nearly randomly. Near random tumbling would tend to average the magnetic anisotropy.

Both dipolar interactions between Mn^{2+} and structural Fe^{3+} and differences in the average Mn^{2+} - Mn^{2+} distances in the a b plane and the c direction appear to contribute to the observed anisotropy. Among the four minerals, hectorite has the lowest Fe^{3+} content (<0.14%). Also, in the air-dried state it exhibits the minimum disparity between Mn^{2+} distances within an interlayer and across interlayers. Consequently, it shows little or no anisotropy in the air-dried, as well as the fully hydrated, state. Air-dried nontronite and the montmorillonites, on the other hand, contain greater amounts of Fe^{3+} (cf., Table 1) and exhibit a greater disparity in exchange ion distances. Thus, these minerals exhibit anisotropic line broadening in the air-dried state. Even in the fully hydrated state, however, the tumbling of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ in nontronite and Chambers montmorillonite does not appear sufficiently random to completely average the anisotropy.

The importance of Mn^{2+} - Fe^{3+} dipolar interactions in the case of Mn^{2+} -nontronite is indicated by line widths which are larger than those for Chambers montmorillonite, despite longer exchange ion

Table 3. ESR line widths of oriented Mn^{2+} -smectites*.

	Interlayer Mn^{2+} - Mn^{2+} distance, Å [†]	Air-Dried Mineral		Fully Hydrated Mineral	
			⊥		⊥
Montmorillonite (Chambers)	10.7	125	110	105	97
Nontronite	11.3	165	148	113	106
Montmorillonite (Upton)	12.0	125	110	89	86
Hectorite	13.6	93	90	75	79

* The widths are the average values in gauss for the $m_I = \pm 5/2$ resonance components with the magnetic field direction oriented || and ⊥ to the crystallographic a b plane.

† This is the average distance between Mn^{2+} ions within an interlayer.

distances in the former mineral. Their importance is further underscored in the dehydrated mineral where the ion occupies a hexagonal position or a vacant octahedral site very near Fe^{3+} in the silicate structure. Under these conditions, the lines are so broadened that they are not detectable. There is little doubt that much of the line broadening observed on passing from fully hydrated to air-dried and thermally dehydrated nontronite is due to increasing dipolar interactions with Fe^{3+} as the Mn^{2+} ions move nearer the silicate structure. Similar effects are probably less important but still operative for the montmorillonites. In hectorite, where little Fe^{3+} is present, the increase in line widths with decreasing hydration state can only be interpreted in terms of reduced mobility of the interlayer. However, even in this latter case, it is difficult to assess quantitatively the interlayer mobility, because the line widths are still determined by an interionic dipolar relaxation mechanism involving neighboring Mn^{2+} exchange ions.

In absence of dipolar interactions, spin relaxation of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ in solution results from molecular collisions between the solvated ion and solvent molecules which cause random distortions of the complex and induce a zero field splitting (Rubinstein et al., 1971; Luckhurst and Pedulli, 1971). Under appropriate conditions, it is possible to obtain a quantitative comparison of the correlation time τ for the ion on the exchange surfaces and in bulk solution from the relative esr line widths in the two environments. When $\omega_0\tau \ll 1$, which is generally the case for $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ at room temperature and at X-band frequency ($\omega_0 = 0.58 \times 10^{11}$ radians/sec), the width of the $|-1/2\rangle \longleftrightarrow |+1/2\rangle$ transition is directly proportional to τ and the inner product (D:D)

of the zero field splitting tensor (Burlamacchi, 1971; Burlamacchi et al., 1970). Therefore, if the reasonable assumption is made that (D:D) is the same in bulk solution and on the exchange surfaces of the mineral, then the relative correlation times should be directly proportional to the ratio of line widths.

Dipolar interactions between $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ ions in hectorite were eliminated by doping a Mg^{2+} exchange form of the mineral with 5% Mn^{2+} . As illustrated in Figure 4 a, the doped sample exhibits six, almost fully resolved hf lines under fully hydrated conditions. The width of the fourth highest field component at room temperature, which is a reliable estimate of the width of the $|+1/2\rangle \longleftrightarrow |-1/2\rangle$ transition (Garrett and Morgan, 1966), is 28.7 G. In comparison, the width of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ in dilute aqueous solution at room temperature is 22 G. Therefore, the value of τ , which can be taken physically to be the precollision lifetime of the ion (Rubinstein et al., 1971), is only ca. 30% longer in the interlayer than in bulk solution where it has been estimated to be 3.2×10^{-12} sec. (Rubinstein et al., 1971). Thus, the interlayer of the fully hydrated mineral is indeed very much solution like. In contrast, τ for $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ has been estimated to be ca. 2.2 times larger in three-dimensional synthetic zeolites than in bulk solutions (Tikhomirova et al., 1973).

Intuitively, drying the mineral down to two molecular layers of water should cause the mobility of the interlayer to decrease. This is confirmed by an increase in the line widths for the doped mineral as illustrated in Figure 4 b. However, the lines are too broad and

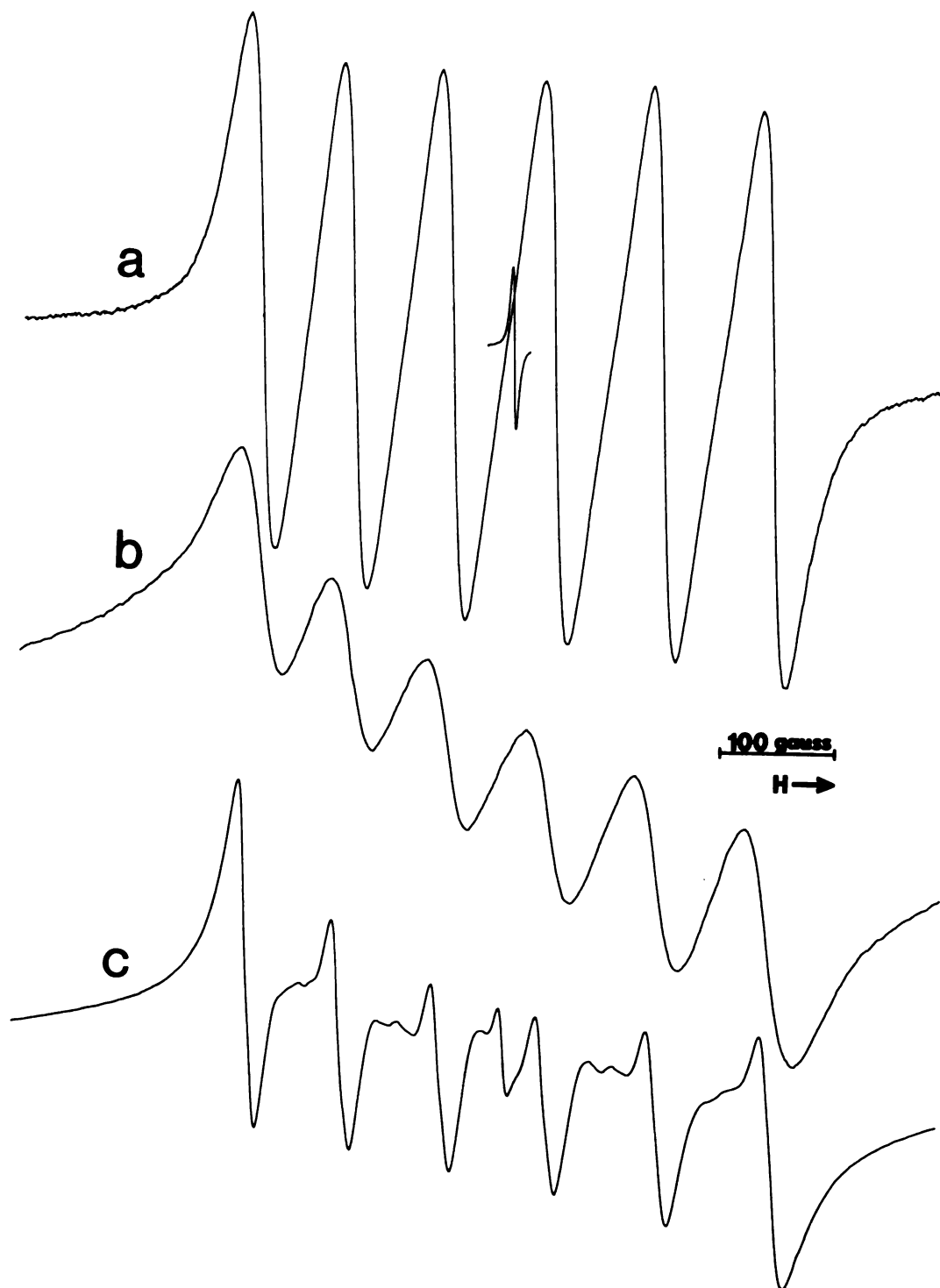


Figure 4. Room temperature esr spectra of powder samples of 5% Mn^{2+} -doped Mg^{2+} -hectorite a) fully hydrated, b) air-dried, and c) thermally dehydrated at 200°C .

overlapping (average width 48 G) to obtain a simple quantitative estimate of the $|-1/2\rangle \longleftrightarrow |+1/2\rangle$ transition (Burlamacchi et al., 1973).

Figure 4 c shows the spectrum of the doped mineral under thermally dehydrated conditions where the interlayers are collapsed and the Mn^{2+} ions are coordinated to silicate oxygens in hexagonal positions. The spectrum consists of six main lines which represent the allowed $\Delta m_I = 0$ transitions and five pairs of weaker doublets which are due to forbidden transitions with $\Delta m_I = \pm 1$. This type of spectrum is characteristic of Mn^{2+} in certain crystalline matrices and in frozen glasses in absence of dipolar coupling (Allen and Nebert, 1964). Thus, as expected under anhydrous conditions, there is no solution character to the interlayer Mn^{2+} ions.

Conclusions

Because of the short exchange ion distances and the presence of structural Fe^{3+} in most smectite minerals, the esr line widths of interlayer Mn^{2+} ions under hydrated and anhydrous conditions is controlled by anisotropic dipolar coupling between paramagnetic centers. In the case of hectorite, which has a low Fe^{3+} content, Mn^{2+} - Mn^{2+} interactions can be eliminated by doping Mn^{2+} into a diamagnetic Mg^{2+} exchange form of the mineral. When the mineral is fully hydrated with the $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ ions in ca. 12.5Å interlayers containing several molecular layers of water, the interlayers are very much solution-like with the mean lifetime between ion-solvent collisions only slightly longer than found for bulk solutions. Under air-dried conditions, where the $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ ions are

sandwiched between silicate sheets in interlayers two molecules of water thick, the interlayers are still solution-like but considerably less mobile than bulk solutions. Thermal dehydration transforms the solution-like esr spectrum into one characteristic of the solid state as the Mn^{2+} ions move into hexagonal arrays of oxygen atoms in the silicate structure.

PART III

EXCHANGE ION POSITIONS IN SMECTITE: EFFECTS ON
ELECTRON SPIN RESONANCE OF STRUCTURAL IRON

The positions of exchange ions in smectite minerals depend in part on the hydration energies of the cations and hydration conditions. Under ambient conditions, they may be solvated by one or two molecular layers of water as in $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ and $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, (Clementz et al., 1973), whereas in the wet silicate they are generally present in greatly expanded interlayers as fully hydrated cations. Thermal dehydration of the cations allows the silicate layers to collapse as the ions move into hexagonal cavities formed by oxygen atoms on the interlayer surfaces. In these hexagonal sites, the dehydrated cations are adjacent to structural OH groups (McBride and Mortland, 1974). Since the dioctahedral smectites possess vacant octahedral positions, small cations such as Li^+ can migrate irreversibly at sufficiently elevated temperatures through the hexagonal cavities into the empty octahedral sites (Calvet and Prost, 1971). The present work demonstrates that the position of the interlayer cation can be readily determined from the nature of the electron spin resonance (esr) signals of Fe^{3+} ions present in the aluminosilicate layers of the mineral.

Isolated structural Fe^{3+} ions in distorted tetrahedral or octahedral sites of silicate minerals (Matyash et al., 1969; Kemp, 1971; Novozhilov et al., 1970) and glasses (Castner et al., 1960) commonly exhibit a broad signal with an isotropic g value near 4.3. Hydrated Na^+ , Li^+ and Ca^{2+} exchange forms of the smectite in this study (Upton, Wyoming montmorillonite, $\text{M}_{0.64}^+(\text{Al}_{3.06} \text{Fe}_{0.32} \text{Mg}_{0.66}) (\text{Al}_{0.10} \text{Si}_{7.90})$

$\text{O}_{20}(\text{OH})_4$ exhibits two Fe^{3+} signals near $g = 4.9$ as shown in Figure 1.1. Since the distribution of Al^{3+} , Fe^{3+} and Mg^{2+} in two-thirds of the octahedral positions is random and the $\text{Al}^{3+}/\text{Mg}^{2+}$ ratio is 4.64, Fe^{3+} in octahedral positions formed by sharing edges with octahedra containing Al^{3+} should be almost five times more likely than Fe^{3+} ions which share edges with Mg^{2+} . The Mg^{2+} ions are the source of net negative charge in the silicate structure, and this charge imbalance must cause the Fe^{3+} environment adjacent to Mg^{2+} to differ from those adjacent to Al^{3+} . Thus, the stronger Fe^{3+} signal is attributed to $\text{Fe}^{3+}\text{-Al}^{3+}$ pairs with orthorhombic symmetry (Angel and Hall, 1972), whereas the weaker signal most likely arises from $\text{Fe}^{3+}\text{-Mg}^{2+}$ pairs.

The Fe^{3+} signals for the Na^+ , Li^+ and Ca^{++} exchange forms after dehydration at 205° for 24 hours are illustrated in Figure 1.2. Subsequent to thermal dehydration, the samples were allowed to equilibrate in 95% ethanol to allow re-expansion of the interlayers, and the esr spectra shown in Figure 1.3 were obtained. Even in smectites where irreversible charge reduction takes place by thermal migration of cations into the octahedral position, ethanol is known to effectively expand the collapsed layer silicates (Brindley and Ertem, 1971). The esr results indicate that for the Na^+ and Ca^{2+} smectite, thermal dehydration eliminates the weaker Fe^{3+} signal (indicated by arrows in spectra), while resolution and expansion of the interlayers regenerates this signal. However, the weak esr signal of the dehydrated Li^+ smectite does not return upon solvation. Thermal dehydration of the Na^+ and Ca^{2+} exchange cations allows movement of these ions into hexagonal cavities and the ionic charge to approach the source of negative charge on

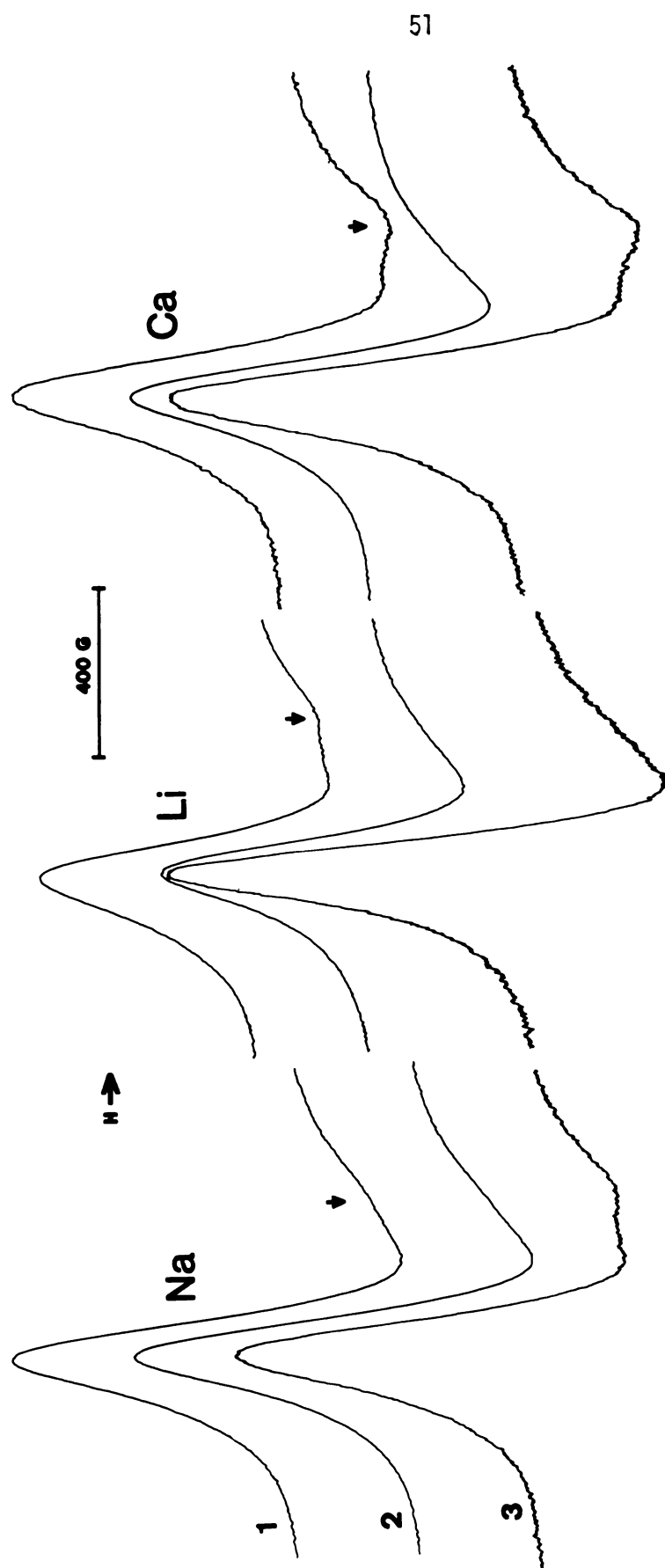


Figure 1. Effects of thermal dehydration and resolution of Na⁺, Li⁺, and Ca²⁺ smectites on the esr signal of structural Fe³⁺.

1. Hydrated mineral under ambient conditions
2. Mineral dehydrated at 205°C for 24 hours
3. Mineral resoluted in ethanol after 205° heat treatment

The arrows indicate the weak Fe³⁺ resonance.

oxygens associated with structural Mg^{2+} . Therefore, the $\text{Fe}^{3+}\text{-Mg}^{2+}$ pairs will no longer experience charge imbalance and will become more like $\text{Fe}^{3+}\text{-Al}^{3+}$ configurations which possess no net charge. Dehydration may then cause the weak Fe^{3+} resonance of $\text{Fe}^{3+}\text{-Mg}^{2+}$ pairs to shift into the invariant strong resonance as the environments of Fe^{3+} in $\text{Fe}^{3+}\text{-Mg}^{2+}$ and $\text{Fe}^{3+}\text{-Al}^{3+}$ pairs become more alike. Resolvation of the mineral in ethanol simply reverses the effects of dehydration as evidenced by the reappearance of the weak Fe^{3+} resonance. The Ca^{2+} and Na^{+} ions move out of their hexagonal cavities due to their energy of solvation, and this ion migration reestablishes the non-equivalence between $\text{Fe}^{3+}\text{-Al}^{3+}$ and $\text{Fe}^{3+}\text{-Mg}^{2+}$ pairs.

In the case of Li^{+} smectite, the exchange ions are small enough to migrate irreversibly into vacant octahedral sites of the silicate at elevated temperature and solvation in ethanol does not restore the weak Fe^{3+} signal. The resulting $\text{Li}^{+}\text{-Fe}^{3+}\text{-Mg}^{2+}$ configurations have no imbalance. Apparently, both silicate charge reduction of smectite by Li^{+} ions and movement of dehydrated Ca^{2+} and Na^{+} ions into hexagonal cavities have a very similar effect on the environment of Fe^{3+} associated with charge sites. This result could only occur if both exchange ions in hexagonal cavities and ions that have migrated into octahedral positions are positioned as closely as possible to the oxygens associated with structural Mg^{2+} . The electrostatic attraction between positive exchange ions and the structural negative charge associated with Mg^{2+} insures this positioning.

The tendency for the exchange ions to occupy hexagonal cavities should increase as the electrostatic attraction between the cation and

silicate surface competes more favorably with the hydration energy of the ion. As shown in Figure 2 for K^+ , Na^+ , Li^+ and Ca^{2+} montmorillonite, there is a decrease in the intensity of the weak Fe^{3+} signal as the relative humidity decreases. Also, at a given relative humidity the signal increases with the hydration energy of the exchange ion (-77, -97, -124, and -377 kcal/mole, respectively, for K^+ , Na^+ , Li^+ and Ca^{2+}). Thus, at 0% humidity, K^+ resides exclusively in hexagonal positions, whereas Ca^{2+} remains hydrated in the interlayer. Even at 93% relative humidity, some K^+ and Na^+ appear to be partially dehydrated and in hexagonal sites since the weak Fe^{3+} resonances are less intense than those for the Li^+ and Ca^{2+} exchange forms of the mineral at the same humidity. These results are in qualitative agreement with the distribution of exchange cations calculated from hydration energies and the charge densities of layer silicates (Shainberg and Kemper, 1966).

The weak resonance of structural Fe^{3+} , because of its apparent sensitivity to cationic charge in the hexagonal cavities, may also be useful to determine the degree of "keying" of organic cations into the silicate structure. For example, a smectite exchanged with tetramethylammonium ions and dehydrated by heating to 110°C retained most of its weak Fe^{3+} resonance, whereas a similarly dehydrated methylammonium smectite lost much of the weak signal intensity. The latter result supports the earlier suggestion that the $(CH_3)_3NH_3^+$ ions key into the hexagonal cavities adjacent to structural Mg^{2+} (Gast and Mortland, 1971). Steric factors, however, prevent keying of the $(CH_3)_4N^+$ ion.

Further esr studies of structural Fe^{3+} in other organic and inorganic cation exchange forms of smectite should supply additional

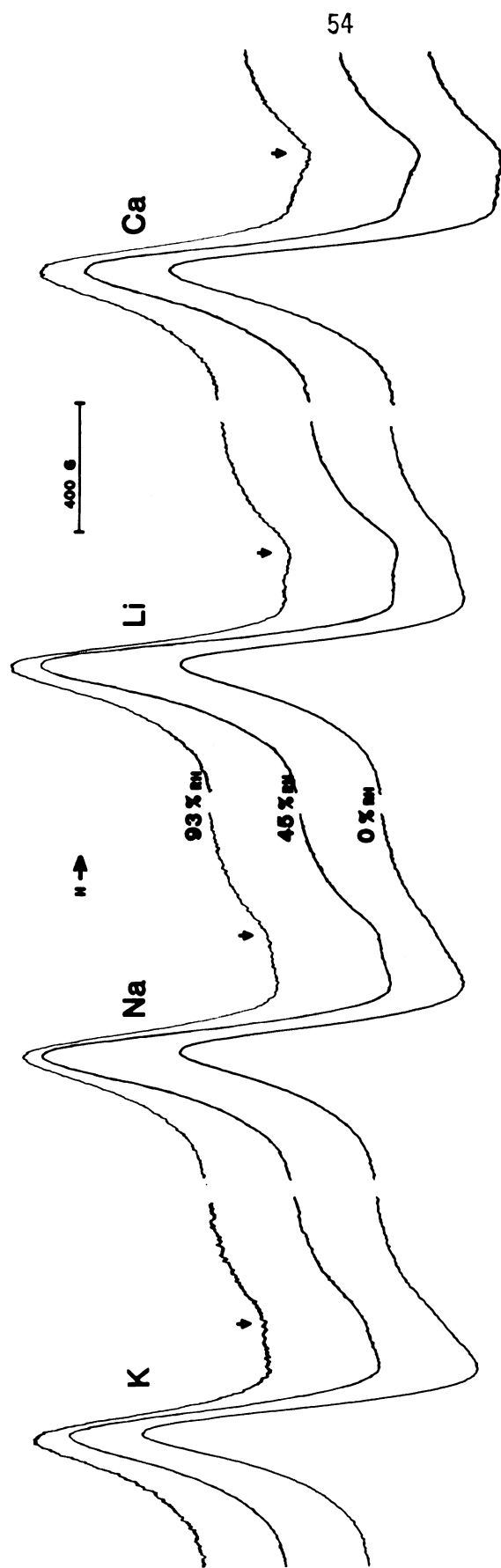


Figure 2. The Fe(III) esr signal of K⁺, Na⁺, Li⁺, and Ca²⁺ smectites after equilibration at various relative humidities (RH). (The upper, middle, and lower spectra are for 93%, 45%, and 0% RH, respectively.) The arrows indicate the weak Fe³⁺ resonances.

useful information on the position and orientation of the ions on the interlayer surfaces.

PART IV

PERTURBATION OF STRUCTURAL Fe^{3+} IN SMECTITES BY EXCHANGE IONS

Introduction

Exchange cations in the interlamellar regions of layer silicates are known to vary their positions relative to the silicate surface depending upon the cationic species and the hydration state of the mineral. For example, an air-dry K^+ -montmorillonite is largely collapsed (10 Å basal spacing) with potassium ions embedded in the hexagonal cavities of the surface structural oxygen atoms (Grim, 1968a). In contrast, montmorillonite exchanged with a strongly solvating cation such as Mg^{2+} has an air-dry basal spacing of 14.5-15.0 Å, indicating a double layer of interlamellar water formed by $Mg(H_2O)_6^{2+}$ ions (Walker, 1955). Thus, the Mg^{2+} ions are in the center of the interlayer. By heating strongly hydrated clays to near 200°C, most of the ligand water is removed and the cations then enter hexagonal cavities of the structure, allowing total collapse of the montmorillonite to a basal spacing of about 9.7 Å (McBride and Mortland, 1974). In these positions, the cations perturb structural hydroxyls, and it has been possible to correlate changes in the structural OH stretch and deformation bands in the infrared region with the state of dehydration of the mineral (Russell and Farmer, 1964; McBride and Mortland, 1974).

Recently, the electron spin resonance (esr) of Upton, Wyoming montmorillonite (and several other layer silicates) near $g = 4.9$ has been assigned to structural Fe^{3+} of orthorhombic sites in the octahedral layer (McBride et al., 1974; Angel and Hall, 1972). The $g = 4.9$ signal

appears to be composed of two resonances: a low-field strong resonance that is invariant, and a slightly higher field overlapping resonance that is eliminated in montmorillonites by dehydration (McBride *et al.*, 1974). The high-field signal is considered to be produced by Fe^{3+} adjacent to octahedral Mg^{2+} . Since isomorphous substitution of Al^{3+} by Mg^{2+} produces most of the layer charge in montmorillonite, the high-field Fe^{3+} is adjacent to unbalanced negative charge and, therefore, resonates at a different position from the Fe^{3+} next to octahedral Al^{3+} . However, dehydration of the clay allows exchange cations to enter hexagonal holes near octahedral Mg^{2+} and balance the negative layer charge. As a result, the structural $\text{Fe}^{3+}\text{-Mg}^{2+}$ group no longer experiences unbalanced negative charge and resonates at a lower magnetic field position, similar to Fe^{3+} adjacent to structural Al^{3+} ($\text{Fe}^{3+}\text{-Al}^{3+}$). Thus, the appearance or disappearance of the high-field Fe^{3+} resonance can be used to determine cation position relative to the silicate surface under various conditions of hydration. The objective of this study is to evaluate the usefulness of Fe^{3+} esr in describing the migration of different cations as the solvent content of interlayers is varied, and to compare esr results with evidence from infrared spectroscopy.

Methods

An Upton, Wyoming montmorillonite was used in all experiments, having the chemical formula: $\text{M}_{0.64}^+ [\text{Al}_{3.06} \text{Fe}_{0.32} \text{Mg}_{0.66}] (\text{Al}_{0.10} \text{Si}_{7.90}) \text{O}_{20} (\text{OH})_4$ (Ross and Mortland, 1966). Various exchange forms were obtained by washing the $<2\mu$ fraction in large quantities of aqueous chloride solution, followed by dialysis of the clay suspension until the

AgNO_3 test showed no evidence of chloride. The proton-exchanged clay was prepared by passing a Na^+ -montmorillonite suspension through a protonated resin column (Amberlite IR-120) and drying immediately at room temperature by boiling off the water under vacuum.

Infrared spectra of self-supporting clay films were obtained on the Beckman IR-7 spectrophotometer. These films were mounted in a specially designed brass cell with NaCl windows to allow degassing and heating to 110°C , so that infrared spectra of dehydrated clays could be obtained.

Electron spin resonance spectroscopy of clay powders was done in quartz tubes using a Varian E4 spectrometer. Spectra of dehydrated clays were obtained by heating the clay powders in quartz tubes and immediately sealing the tubes to prevent rehydration during the recording of spectra.

Discussion of Results

The esr of Fe^{3+} near $g = 4.9$ shows changes which can be correlated to the solvation state of the montmorillonite. For example, an air-dry Ca^{2+} -clay demonstrates a relatively intense high-field Fe^{3+} signal indicated by the arrow in Figure 1 A. The basal spacing of this clay is $14.9 \text{ \AA}$, indicating a double layer of interlamellar water molecules, and the high-field signal is evidence that the Ca^{2+} ions are not in hexagonal cavities of the silicate surface but are positioned in the center of the interlamellar region as $\text{Ca}(\text{H}_2\text{O})_6^{2+}$ species (McBride *et al.*, 1974). In contrast, the loss of the high-field Fe^{3+} signal upon dehydration of the clay (Figure 1 B) indicates that the Ca^{2+} ions have entered

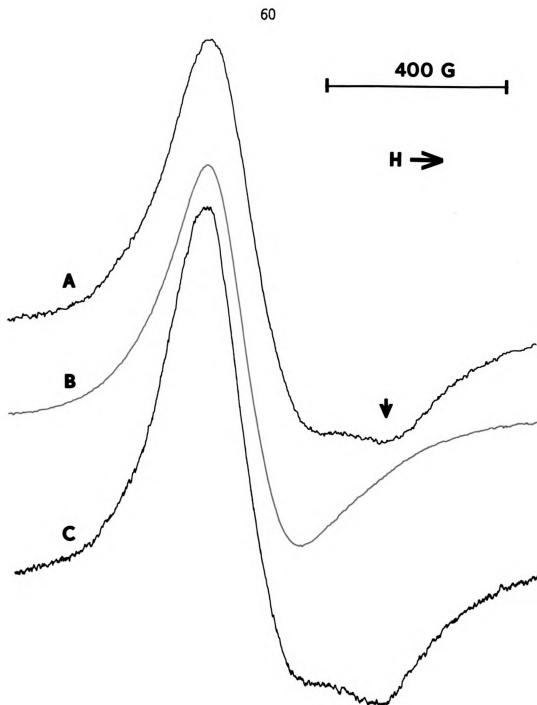


Figure 1. Structural Fe^{3+} esr spectra of Ca^{2+} -montmorillonite.

- A. air-dry
- B. heated at 210°C for 24 hours
- C. resolvated in 95% ethanol after 210°C thermal treatment

the hexagonal cavities of the collapsed interlayers ($9.7 \text{ \AA}$ basal spacing) and are compensating the negative charge associated with octahedral Mg^{2+} . Resolution of the dehydrated Ca^{2+} -montmorillonite in 95% ethanol expands the interlayers ($17.0 \text{ \AA}$ basal spacing), and the high-field signal reappears as the Ca^{2+} ions resolvate and move out of the hexagonal holes (Figure 1 C).

Since the high-field Fe^{3+} is sensitive to the distance between the source of layer charge and the compensating cation, clay samples were exchanged with several metal and alkylammonium cations of different sizes in order to vary this distance. These clays were fully dehydrated by heating before esr spectra were obtained. The spectra were analyzed by integrating the areas of the main Fe^{3+} resonance and the weaker high-field Fe^{3+} resonance and utilizing the ratio of these two areas as an indicator of the relative quantity of Fe^{3+} unperturbed by interlayer cations. For example, the Ca^{2+} -montmorillonite expanded in 95% ethanol possesses a strong high-field resonance (Figure 1 C) which is measured as a high ratio (Figure 2) because of little interaction between fully solvated Ca^{2+} and the silicate. Dehydrating the clay by heating eliminates the high-field Fe^{3+} signal (Figure 1 B); the ratio is then zero (Figure 2). Therefore, signal ratios close to zero indicate strong interaction between interlayer cations and sites of negative charge in the layer silicate.

The esr spectra are first derivatives of the absorption spectra, so that areas beneath peaks do not directly give signal intensities. However, intensities are generally determined fairly accurately as $(\text{signal width})^2 \times (\text{signal height})$ (Levanon and Luz, 1968). Since the

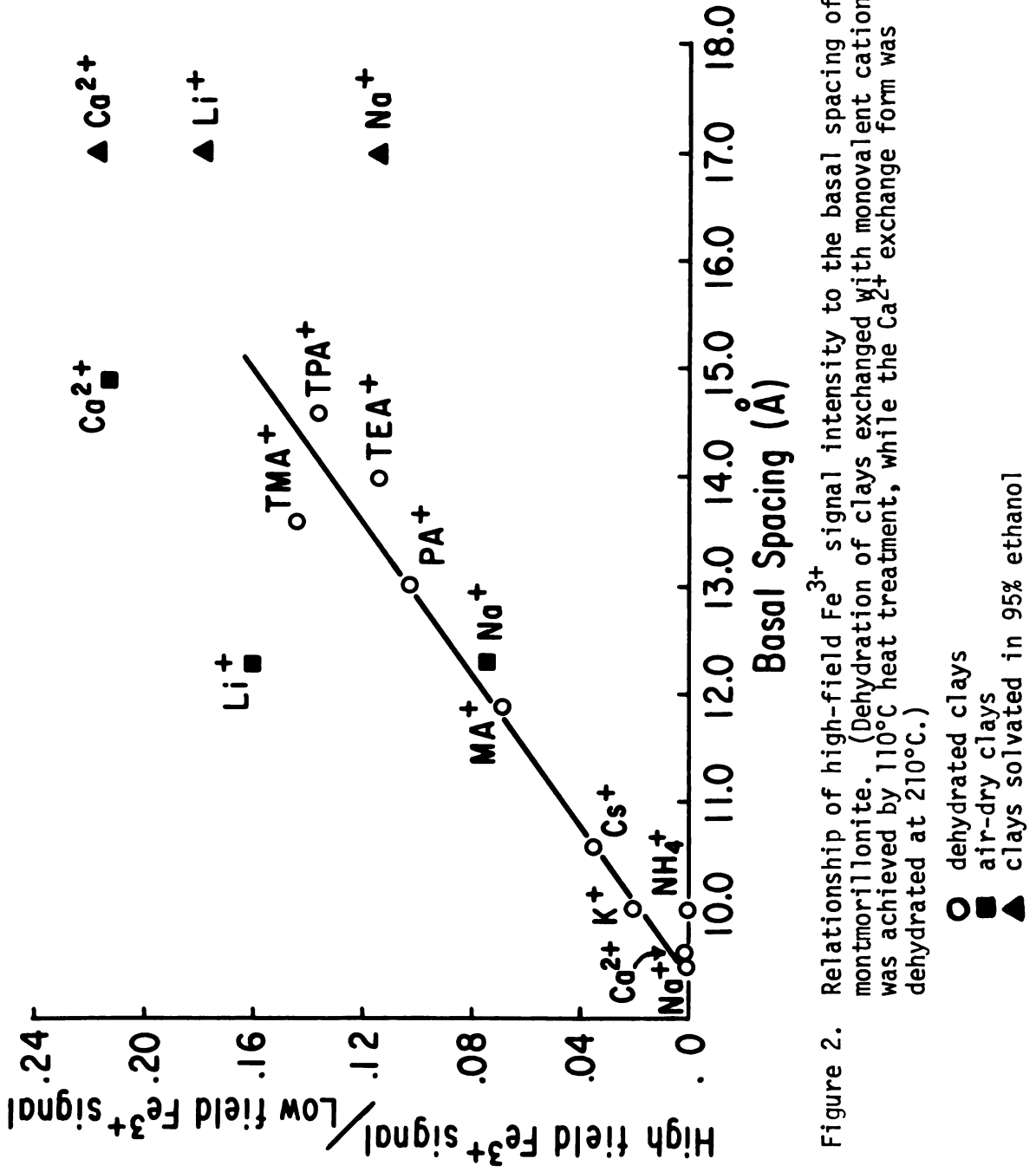


Figure 2. Relationship of high-field Fe^{3+} signal intensity to the basal spacing of montmorillonite. (Dehydration of clays exchanged with monovalent cations was achieved by 110°C heat treatment, while the Ca^{2+} exchange form was dehydrated at 210°C .)

- dehydrated clays
- air-dry clays
- ▲ clays solvated in 95% ethanol

two Fe^{3+} signals partially overlap, the relative intensity of the high-field Fe^{3+} resonance can only be estimated by measuring the area added to the lower-field Fe^{3+} signal by the high-field shoulder (indicated by the arrow in Figure 1). The strength of the lower-field signal is arbitrarily taken as the area under the peak and above the horizontal baseline. This area represents an internal standard of structural Fe^{3+} content. For signals of fairly constant width, first derivative signal areas should be proportional to relative intensities.

In Figure 2, the relationship between the basal spacing of dehydrated clays and the ratio of Fe^{3+} signal areas is apparent. The Na^+ , K^+ , NH_4^+ , and Cs^+ -montmorillonites were dehydrated by 110°C heat treatment and the Ca^{2+} -montmorillonite was dehydrated at 210°C. The very low relative intensity of the high-field Fe^{3+} signal in these clays indicates that the cations are embedded in the hexagonal cavities of the silicate surface. The Cs^+ ions, being too large to fully enter the hexagonal holes, prevent the silicate layers from totally collapsing to 9.5-9.7 Å, and cannot quite fully eliminate the high-field signal. Clays exchanged with organic cations are dehydrated by 110°C heat treatment. The high-field signal becomes more intense as the interlamellar organic cations hold the layers further apart, a result expected from the position of cationic charge (Figure 2). Steric hindrance prevents the positive charge of tetraalkylammonium ions from approaching closely, or entering, hexagonal cavities of the montmorillonite. Methylammonium (MA^+) and propylammonium (PA^+) ions may "key" into the hexagonal holes to some extent (Gast and Mortland, 1971), but the presence of high-field Fe^{3+} indicates that the methyl and propyl groups attached to the

$-\text{NH}_3^+$ group prevent the latter from fully penetrating into the structure. In contrast, dehydrated NH_4^+ -montmorillonite shows no high-field Fe^{3+} (Figure 2), a result of more complete penetration of the structure. In summary, the dehydrated clays substituted with organic and inorganic cations reveal a direct relationship between the relative intensity of the high-field Fe^{3+} signal and the basal spacing (indicated by the line in Figure 2). This relationship is evidence of decreased perturbation of structural Fe^{3+} associated with structural Mg^{2+} as the charge of the cation is moved further from the silicate surface.

The presence of solvent molecules in the interlamellar regions greatly influences the position of cations relative to the surface. As previously described, Ca^{2+} ions in air-dry montmorillonite are separated from the surfaces by water molecules as evidenced by the strong high-field Fe^{3+} signal. The air-dry Li^+ -clay, with a basal spacing of $12.3 \text{ \AA}$, has a monolayer of water in the interlayer. The high-field signal, although less intense than in the Ca^{2+} -clay, is strong enough to indicate that the Li^+ ions are not in hexagonal holes (Figure 2). This result is consistent with the concept of coordination of three water molecules to Li^+ so that the exchange cations are near the middle of the interlayer (Grim, 1968b). In contrast, the air-dry Na^+ -clay has a much weaker high-field signal despite the fact that the basal spacing is also $12.3 \text{ \AA}$. The Na^+ ions must be partially dehydrated and close to hexagonal cavities; a portion of the ions may actually penetrate the cavities. These observations agree qualitatively with calculations of expected cation positions on clay surfaces based on the known hydration energies of Ca^{2+} , Na^+ , and Li^+ (Shainberg and Kemper, 1966). Clays fully solvated in 95% ethanol

(17.0 Å basal spacing) show the expected direct relationship of the hydration energy of interlayer cations to the intensity of high-field Fe^{3+} (Figure 2). The signal intensity increases in the order $\text{Na}^+ < \text{Li}^+ < \text{Ca}^{2+}$, evidence that the strongly solvated Ca^{2+} tumbles freely in the expanded interlayer, while Li^+ associates more closely with the surface, and more weakly solvated Na^+ tends to approach the surface most readily.

An interesting observation from Figure 2 is that the air-dry and solvated montmorillonites have high-field Fe^{3+} signal intensities that do not generally plot near the line defined by dehydrated clays. For example, air-dry Li^+ and Ca^{2+} -clays have high-field signals that are more intense than those present in organic-exchanged clays possessing similar basal spacings, despite the fact that the former clays do not have any greater separation of the cation charge from the silicate surface than the latter. This result may be a reflection of the effective dielectric constant of the interlayer. The electrostatic force of attraction between an interlayer cation and a site of negative charge on the silicate can be expressed as: $f = \frac{q_1 q_2}{E r^2}$ where q_1 and q_2 represent the positive and negative charges, E is the dielectric constant of the interlayer, and r is the distance between q_1 and q_2 . For clays with large organic cations (and no water) in the interlayers, E should be quite low so that the attractive force between the cations and the silicate surface is relatively high. Thus, the energy of cation-silicate interaction is reflected in the perturbation of structural Fe^{3+} with some loss of the high-field Fe^{3+} signal. The Na^+ , Li^+ and Ca^{2+} clays with water or ethanol molecules occupying the interlayers demonstrate a stronger high-field Fe^{3+} signal because E is large and the force of

attraction between the cation and the silicate surface is reduced by dielectric "shielding" (Figure 2). Evidence from infrared spectroscopy indicates that dielectric links of water or alcohol molecules form between the cations and negatively charged surface oxygens, resulting in lowered electrostatic energy (Farmer and Russell, 1971). Thus, "shielding" of the cation from the silicate structure apparently results from orientation of solvent molecules into coordination and hydrogen-bonding arrangements between the cation and the silicate.

In the dehydrated montmorillonites of Figure 2, the interlayer dielectric constants should all be low and relatively constant, so that the electrostatic energy of attraction will vary as $\frac{1}{r}$. Since r is proportional to the basal spacing, the direct relationship between basal spacings of the clays and the strength of the high-field Fe^{3+} signal simply reflects the dependence of electrostatic interaction on the distance between charge sites of the cation and the silicate.

Protons on exchange sites should affect the Fe^{3+} esr signal much like larger cations such as Li^+ and Na^+ . A freshly prepared H_3O^+ -montmorillonite shows a slight high-field Fe^{3+} signal when air-dry (Figure 3 A) as would be expected for H_3O^+ ions close to the silicate surfaces. When this clay is heated to 225°C , the high-field signal cannot be observed (Figure 3 B), suggesting that the protons have penetrated the hexagonal holes of the structure upon dehydration. Protons of H_3O^+ -montmorillonite are known to migrate to structural OH groups associated with Mg^{2+} (Russell and Fraser, 1971; Yariv and Heller-Kallai, 1973). This process is especially pronounced when dehydration by heating decomposes the hydronium ions, and the bare protons easily migrate

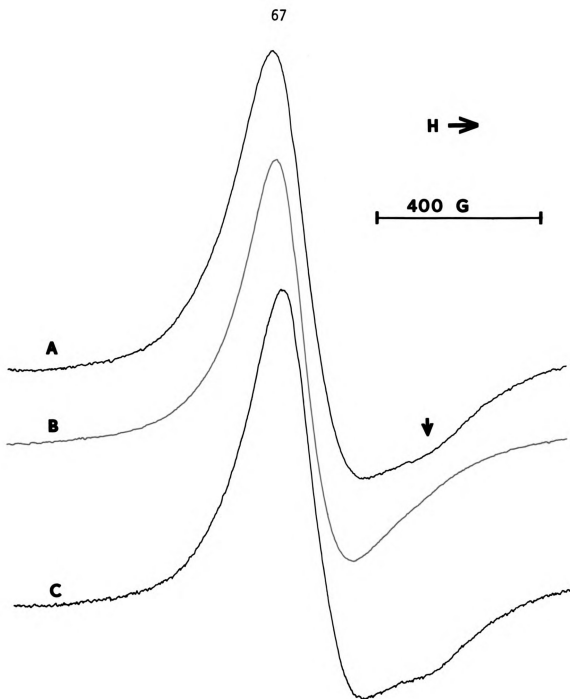


Figure 3. Structural Fe^{3+} esr spectrum of freshly-prepared H_3O^+ -montmorillonite.

- A. air-dry
- B. heated at 225°C for 30 minutes
- C. resolvated in 95% ethanol after 225°C thermal treatment

through surface hexagonal holes to the source of negative charge--hydroxyl groups and oxygen atoms coordinated to octahedral Mg^{2+} . As Figure 3 C shows, the process is reversible with resolution of the interlayers since the high-field Fe^{3+} signal is regenerated to at least the intensity of the air-dry clay. However, the relatively low intensity of this signal in the fully solvated clay is evidence that H_3O^+ ions in expanded interlayers associate closely with the silicate surface, or alternatively some protons remain in the structure. The position of the interlayer protons is dependent on the relative basicity of sites competing for the protons (Mortland, 1966). Apparently, water has some success as a Brönsted base in removing protons associated with the negatively charged sites of the silicate.

Changes in the deformational vibration frequency of structural OH groups associated with Al^{3+} - Mg^{2+} pairs in the octahedral layer, accompany the dehydration of montmorillonite, as cations migrating into hexagonal holes perturb these groups (Russell and Farmer, 1964; McBride and Mortland, 1974). Since these hydroxyls are positioned at the major sites of negative charge in the structure, cations approach the hydroxyls and shift the 847 cm^{-1} band to higher energy (McBride and Mortland, 1974). In Figure 4, the relationship between cation size and degree of perturbation of the hydroxyls in dehydrated montmorillonites is shown. Obviously, large cations such as tetramethylammonium (TMA^+) cannot enter the hexagonal holes, so the OH deformation appears at the unshifted 847 cm^{-1} position. Smaller cations such as Na^+ enter the hexagonal holes when hydration water is removed and shift the band to higher energy. It is apparent from Figure 4 that cations such as Cs^+ have little effect on

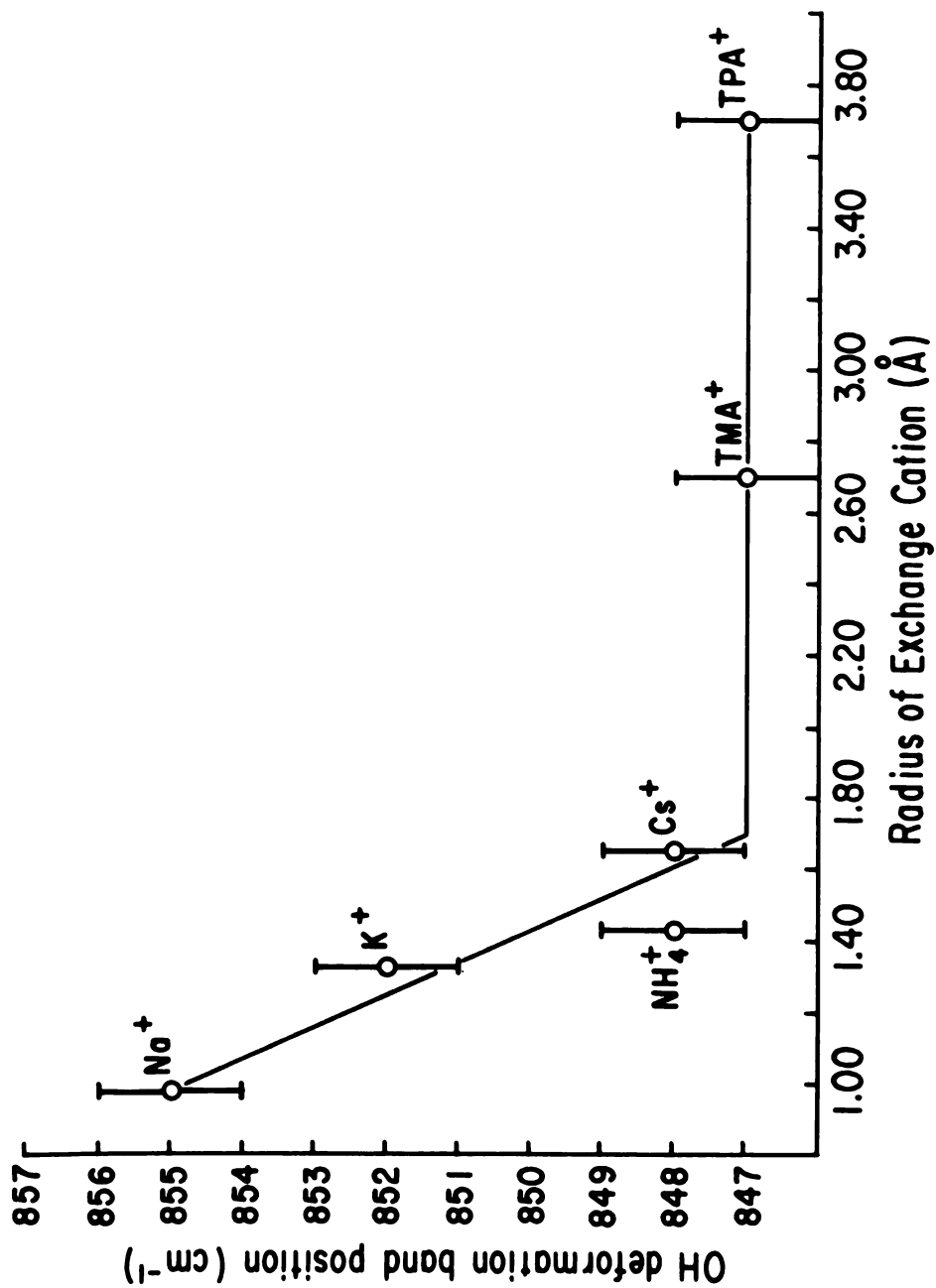


Figure 4. Relationship of the size of interlayer cations to the position of the structural OH deformation band. (All clays are dehydrated by degassing and heating to 110°C.)

the hydroxyls because they are too large to penetrate the hexagonal holes. At the same time, dehydrated Cs^+ -clay demonstrates almost no evidence of a high-field Fe^{3+} signal (Figure 2), indicating that the cation is able to balance the structural charge without closely approaching the octahedral layer through hexagonal holes. This result suggests the importance of oxygen atoms of the tetrahedral layer in delocalizing and conveying octahedral charge through the structure. On the other hand, the interpretations of esr and infrared spectra require that discrete charge sites exist within the octahedral layer. Certainly, charge density is not "smeared" uniformly throughout the layer silicate structure.

Although the positions of univalent cations in dehydrated clay structures can be determined by Fe^{3+} esr and infrared spectroscopy techniques, divalent cations present a problem. A divalent cation must balance two structural charge sites simultaneously, a problem that is overcome in hydrated interlayers because the dielectric medium reduces the electrostatic energy of the system while the hydration sphere maintains the cation at a distance from the silicate surface. However, when interlayer water is removed from Ca^{2+} -montmorillonite by heating to 200°C , the basal spacing collapses to about $9.7 \text{ \AA}$. The Ca^{2+} ions must now occupy hexagonal cavities and the 847 cm^{-1} hydroxyl band is shifted upward to $855\text{--}860 \text{ cm}^{-1}$ by close approach of the cation to the OH groups associated with structural Mg^{2+} . In addition, a weak, lower energy peak near the strong OH stretch at 3630 cm^{-1} appears in the spectrum and is assigned to the same structural hydroxyls (Russell and Farmer, 1964). Dehydrated Na^+ -montmorillonite does not have the subsidiary OH stretch, a result attributed to decreased perturbation of OH

groups by monovalent cations in hexagonal holes. Thus, infrared spectroscopy locates divalent cations in hexagonal holes where simultaneous approach to two silicate charge sites is not possible. Yet, Fe^{3+} esr indicates that structural charge sites are effectively balanced by Ca^{2+} ions in hexagonal holes (Figure 2). Although rapid oscillation of Ca^{2+} between hexagonal holes of adjacent silicate surfaces might explain these results, the process is unlikely because hexagonal holes close to structural charge sites cannot always line up across collapsed interlayers.

Another mechanism of divalent charge separation arises from the increased polarization of water molecules as interlayer water content is lowered. The last few water molecules coordinated to divalent cations are very acid in dry clay systems because of the strong ion-dipole interactions (Mortland and Raman, 1968). Extending this concept further, when only one water molecule is coordinated to Ca^{2+} in the collapsed montmorillonite, the water may be totally dissociated. The following hydrolysis reaction may thus occur: $\text{Ca}(\text{H}_2\text{O})^{2+} \rightarrow \text{Ca}(\text{OH})^+ + \text{H}^+$. The proton so produced may easily migrate through the silicate to the nearest neighboring charge site while the OH^- of $\text{Ca}(\text{OH})^+$ occupies a site formed by hexagonal holes of adjacent silicate surfaces. This mechanism explains the effective neutralization of octahedral charge as observed by esr, while the divalent charge localized on Ca^{2+} causes the perturbation of structural OH that is greater than that for Na^+ -clay. Structural OH groups approached by protons are so influenced as to demonstrate no observable OH deformation band (Yariv and Heller-Kallai,

1973). The proposed mechanism should be reversible so that rehydration of the clay reverses the equation described above.

Fully collapsed Na^+ and Ca^{2+} -montmorillonites exhibit H_2O deformation bands at $1630\text{--}1640\text{ cm}^{-1}$, indicating that some water is trapped in interlayer regions of the structure. This water is obviously not dissociated despite the dehydrating conditions, and may be embedded in hexagonal holes not containing exchange cations.

Conclusions

It has been demonstrated that esr of structural Fe^{3+} in montmorillonite can be used to determine positions of interlayer cations. The Fe^{3+} signal near $g = 4.9$ appears in montmorillonites with low Fe^{3+} content, and the high-field resonance that responds to exchange ion position is also present in several montmorillonites. When the cations are solvated and tumbling rapidly in the interlayer, both the cation-silicate separation and the dielectric medium insulate the octahedral source of layer charge. Desolvation of the cations allows them to move into the hexagonal holes closest to structural Mg^{2+} , where they can readily balance the charge of the octahedral layer.

Infrared spectroscopy verifies the assignment of cation position in dehydrated clays. Since divalent cations cannot balance two charge sites simultaneously, protons must be generated by hydrolysis to allow effective charge compensation in the structure. Positions of interlayer cations relative to the silicate surface may determine the exchangeability, diffusion coefficients and other important properties of the cations.

SUMMARY AND CONCLUSIONS

Spectroscopic investigations of Cu^{2+} and Mn^{2+} on exchange sites of smectites indicate that there is no specific adsorption (i.e., chemisorption) of these transition metal cations. They behave as hydrated exchange ions much like non-transition metals. Upon thermal dehydration, these cations are able to enter hexagonal holes of the silicate surfaces or even further penetrate the structure to occupy vacant sites of the octahedral layer. The former process is reversible by rehydration, but the latter process is not reversible.

Studies of the nature of interlamellar water indicate that the interlayers in fully-hydrated smectites are solution-like. The interlayers can be considered to be very concentrated solutions, since the Mn^{2+} - Mn^{2+} distance in a Mn^{2+} -montmorillonite is about $12.0 \text{ \AA}$, equivalent to a very concentrated solution of MnCl_2 . The two-dimensional nature of the interlayers slightly reduces the mobility of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ complexes in fully-hydrated smectite, and greatly reduces the mobility in the air-dry smectite. This result is expected, since the fully-hydrated clay has an interlayer about $10 \text{ \AA}$ thick, while the air-dry smectite has a $5 \text{ \AA}$ interlayer. There is no evidence of an "ice-like" structure which would result in a very high interlayer viscosity. Because of the concentrated nature of the interlayer "solution," a significant portion of the water molecules are strongly bound in ligand

positions; therefore, much of the interlayer water is necessarily structured or ordered by the exchange cations.

The solvation energies of exchange cations determine their positions in interlayers. Strongly solvating cations (e.g., Ca^{2+} , Mn^{2+} , Cu^{2+}) tumble rapidly in fully expanded interlamellar regions, while weakly solvating cations (e.g., Na^+ , K^+ , Cs^+) tend to approach the sites of negative charge in the layer silicate by residing within or near hexagonal holes of the silicate surface. The cation position is a compromise between the energy of solvation (which moves the cation away from the silicate surface) and the electrostatic energy of attraction (which moves the cation toward the surface). The position of exchange cations relative to the silicate surface may greatly affect the mobility and reactivity of these ions.

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