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

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Abstract—The electron spin resonance of some structural Fe^{3+} for montmorillonites having low Fe^{3+} content, is perturbed by electrostatic interaction between exchange cations and structural charge sites. The position of charge centers of organic and inorganic cations in the interlayer can thus be determined at various levels of solvation. Dielectric media between the silicate layers lower the electrostatic attraction between the silicate and the exchange cations. The silicate charge appears to be partially delocalized on structural oxygen atoms as shown by electron spin resonance and i.r. spectroscopy. There is also evidence that divalent exchange cations on dehydrated montmorillonites cause hydrolysis of water; the protons so produced migrate to structural charge sites.

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, 1968). 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 i.r. 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, Kemp, 1971) near $g = 4{\cdot}3$ has been assigned to structural Fe^{3+} of orthorhombic sites in the octahedral layer (McBride *et al.*, 1975; Angel and Hall, 1972). The $g = 4{\cdot}3$ signal appears to be composed of two resonances: a low-field strong resonance that is invariant, and a weak, 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 Fe^{3+}–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+} (Fe^{3+}–Al^{3+}). Thus, the appearance or disappearance of the weak high-field Fe^{3+} resonance can be used to indicate 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 i.r. spectroscopy.

METHODS

An Upton, Wyoming montmorillonite was used in all experiments, having the chemical formula: $M^+_{0{\cdot}64}$ $[Al_{3{\cdot}06}\ Fe_{0{\cdot}32}\ Mg_{0{\cdot}66}]$ $(Al_{0{\cdot}10}\ Si_{7{\cdot}90})\ O_{20}\ (OH)_4$ (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. This method results initially in about 80 and 20 per cent exchangeable H^+ and Al^{3+} respectively as measured by electrometric titrations.

Infrared spectra of self-supporting clay films were obtained on the Beckman IR-7 spectrophotometer. These films were mounted in a specially designed

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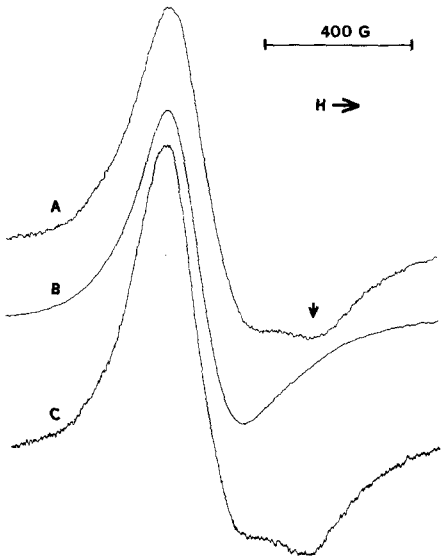


Fig. 1. Structural Fe^{3+} esr spectra of Ca^{2+}–montmorillonite. (A) air-dried. (B) heated at 210°C for 24 hr. (C) resolvated in 95% ethanol after 210°C thermal treatment.

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 $g = 4{\cdot}3$ shows changes which can be correlated with the solvation state of the montmorillonite. For example in air-dried Ca^{2+}–clay demonstrates a relatively intense high-field Fe^{3+} signal indicated by the arrow in Fig. 1A. The basal spacing of this clay is 14·9 Å, 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 $Ca(H_2O)_6^{2+}$ species (McBride *et al.*, 1974). By contrast, the loss of the high-field Fe^{3+} signal upon dehydration of the clay (Fig. 1B) indicates that the Ca^{2+} ions have entered the hexagonal cavities of the collapsed interlayers (9·7 Å basal spacing) and are compensating the negative charge associated with octahedral Mg^{2+}. Resolvation of the dehydrated Ca^{2+}-montmorillonite in 95% ethanol expands the interlayers (17·0 Å basal spacing), and the high-field signal reappears as the Ca^{2+} ions resolvate and move out of the hexagonal holes (Fig. 1C). The same effect is obtained if the clay is resolvated with water.

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 (Fig. 1C) which is measured as a high ratio (Fig. 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 (Fig. 1B); the ratio is then zero (Fig. 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 (signal width) ^{2}X (signal height) (Levanon and Luz, 1968). Since the 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 Fig. 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 Fig. 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

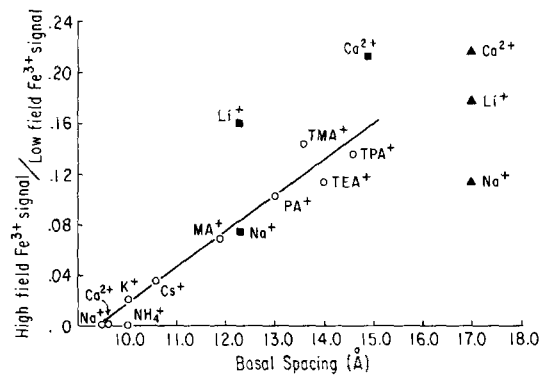


Fig. 2. Relationship of high-field Fe^{3+} signal intensity to the basal spacing of montmorillonite. (Dehydration of clays exchanged with monovalent cations was achieved by 110°C heat treatment, while the Ca^{2+} exchange form was dehydrated at 210°C) ○ dehydrated clays. ■ air-dried clays. ▲ clays solvated in 95% ethanol.

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surface. The Cs^+ ions which are 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 (Fig. 2). Steric hindrance prevents the positive charge of tetra-alkylammonium ions from approaching closely or entering hexagonal cavities of the montmorillonite. Methylammonium (MA^+) and proplyammonium (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 $-NH_3^+$ group prevent the latter from fully penetrating into the structure. In contrast, dehydrated NH_4^+–montmorillonite shows no high-field Fe^{3+} (Fig. 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 Fig. 2). This relationship is evidence of decreased perturbation of structural Fe^{3+} associated with structural Mg^{2+} as the charge center of the cation is moved farther 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-dried montmorillonite are separated from the surfaces by water molecules as evidenced by the strong high-field Fe^{3+} signal. The air-dried Li^+–clay, with a basal spacing of 12·3 Å, 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 (Fig. 2). This result is consistent with the concept of coordination of 3 water molecules to Li^+ so that the exchange cations are near the middle of the interlayer (Grim, 1968). In contrast, the air-dried Na^+–clay has a much weaker high-field signal despite the fact that the basal spacing is also 12·3 Å. 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+} (Fig. 2). The signal intensity increases in the order $Na^+ < Li^+ < Ca^{2+}$, 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 Fig. 2 is that the air-dried 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-dried 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: $f = (q_1 q_2 / Er^2)$ 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" (Fig. 2). Evidence from i.r. 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 Fig. 2, the interlayer dielectric constants should all be low and relatively constant, so that the electrostatic energy of attraction will vary as $1/r$. 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 cations such as Li^+ and Na^+. A freshly prepared H_3O^+–montmorillonite shows a slight high-field Fe^{3+} signal when air-dried (Fig. 3A) 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 (Fig. 3B), 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 through

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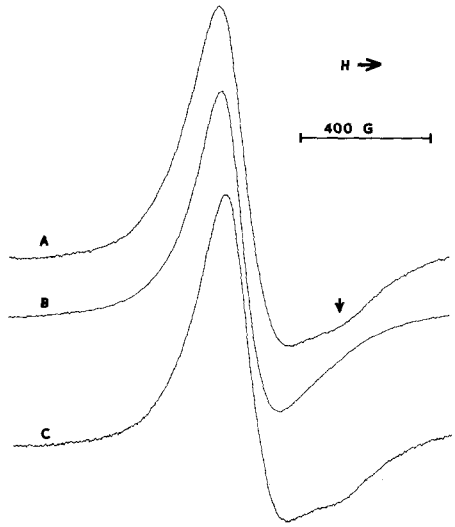


Fig. 3. Structural Fe^{3+} esr spectrum of freshly-prepared H_3O^+–montmorillonite. (A) air-dried. (B) heated at 225°C for 30 min. (C) resolvated in 95% ethanol after 225°C thermal treatment.

surface hexagonal holes to the source of negative charge—hydroxyl groups and oxygen atoms coordinated to octahedral Mg^{2+}. As Fig. 3C shows, the process is reversible with resolvation 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 Fig. 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 Fig. 4 that cations such as Cs^+ have little effect on 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 (Fig. 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 i.r. 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 i.r. 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 surfaces. However, when interlayer water is removed from Ca^{2+}–montmorillonite by heating to 200°C, the basal spacing collapses to about 9·7 Å. The Ca^{2+} ions must now occupy hexagonal cavities and the 847 cm^{-1} hydroxyl band is shifted upward to 855–860 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, i.r. 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 (Fig. 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

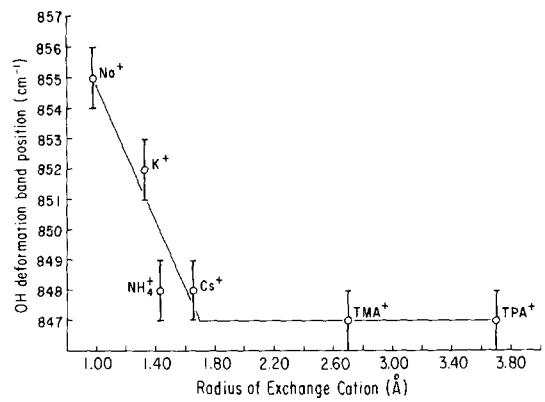


Fig. 4. Relationship of the size of interlayer cations to the position of the structural OH deformation band. (All clays are dehydrated by degassing and heating to 110°C).

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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: $Ca(H_2O) \rightleftarrows Ca(OH)^+ + H^+$. The proton so produced may easily migrate through the silicate to the nearest neighboring charge site while the OH^- of $Ca(OH)^+$ 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 1630–1640 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 $g = 4{\cdot}3$ 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 coeffecients and other important properties of the cations.

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