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

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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 $Cu(H_2O)_4^{2+}$ and $Cu(H_2O)_6^{2+}$ (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, $M^+_{0\cdot64}$ $(Al_{3\cdot06}$ $Fe_{0\cdot32}$ $Mg_{0\cdot66})$ $(Al_{0\cdot10}$ $Si_{7\cdot90})$ $O_{20}(OH)_4)$ exhibit two Fe^{3+} signals near g = 4·4 as shown in Fig. 1(1). The authors suggest that the weak Fe^{3+} resonance may arise from ions adjacent to octahedra containing Mg^{2+}, while the more intense Fe^{3+} resonance is attributed to those ions adjoining octahedra which contain trivalent ions (mainly Al^{3+}). 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 that adjacent to Al^{3+}. Thus the

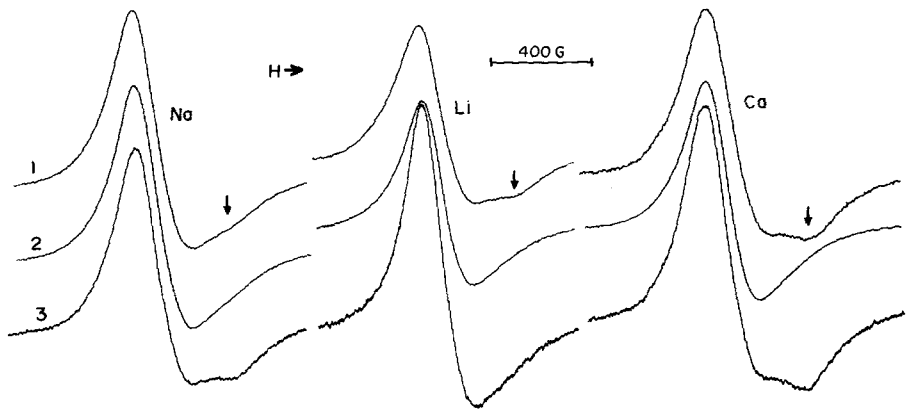

Fig. 1. Effects of thermal dehydration and resolvation of Na^+, Li^+, and Ca^{2+} smectites on the ESR signal of structural Fe^{3+}.

(1) Hydrated mineral under ambient conditions; (2) Mineral dehydrated at 205°C for 24 hr; (3) Mineral resolvated in ethanol after 205° heat treatment.
The arrows indicate the weak Fe^{3+} resonance.

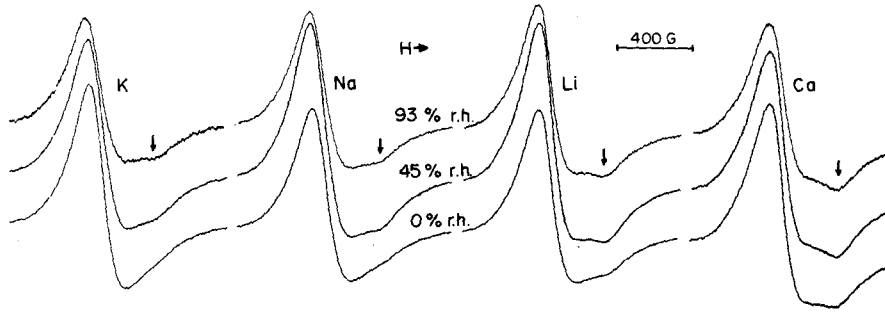

Fig. 2. The Fe(III) ESR signal of K^+, Na^+, Li^+, and Ca^{2+} smectites after equilibration at various r.h. (The upper, middle, and lower spectra are for 93%, 45%, and 0% r.h. respectively.) The arrows indicate the weak Fe^{3+} resonances.

stronger Fe^{3+} signal is attributed to Fe^{3+}–Al^{3+} pairs with orthorhombic symmetry (Angel and Hall, 1972), whereas the weaker signal most likely arises from Fe^{3+}–Mg^{2+} pairs.

The Fe^{3+} signals for the Na^+, Li^+, and Ca^{2+} exchange forms after dehydration at 205°C for 24 hr are illustrated in Fig. 1(2). Subsequent to thermal dehydration, the samples were allowed to equilibrate in 95 per cent ethanol to allow re-expansion of the interlayers, and the ESR spectra shown in Fig. 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 Erterm, 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 resolvation 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 oxygens associated with structural Mg^{2+}. Therefore, the Fe^{3+}–Mg^{2+} pairs will no longer experience charge imbalance and will become more like Fe^{3+}–Al^{3+} configurations which possess no net charge. Dehydration may then cause the weak Fe^{3+} resonance of Fe^{3+}–Mg^{2+} pairs to shift into the invariant strong resonance as the environments of Fe^{3+} in Fe^{3+}–Mg^{2+} and Fe^{3+}–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 re-establishes the non-equivalence between Fe^{3+}–Al^{3+} and Fe^{3+}–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 Li^+–Fe^{3+}–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 cativities 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 Fig. 2 for K^+, Na^+, Li^+ and Ca^{2+} montmorillonite, there is a decrease in the intensity of the weak Fe^{3+} signal as the r.h. 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 per cent humidity, K^+ resides exclusively in hexagonal positions, whereas Ca^{2+} remains hydrated in the interlayer. Even at 93 per cent r.h., 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 $(CH_3)NH_3^+$ 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 useful information on the position and orientation of the ions on the interlayer surfaces.

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INFLUENCE OF CITRIC ACID ON THE CRYSTALLIZATION OF ALUMINUM HYDROXIDES

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Numerous studies have been carried out on the hydrolytic reactions of aluminum at room temperature and pressure in partially neutralized aluminum solutions. These studies have shown that the ionic environment in the system is important in influencing the formation or non-formation of crystalline aluminum hydroxides. Chloride (Hsu, 1966; Turner and Ross, 1970) and SO_4^{-2} (Hsu, 1973) at high concentration and silicic acid (Luciuk and Huang, 1974) will inhibit the formation of crystalline aluminum hydroxides. In soil solutions and natural waters, organic acids form part of the environment and though their concentrations may be low, many of them, e.g. oxalic and citric acids, have strong complexing or chelating properties towards aluminum. It has been reported that non-crystalline hydrous oxides and hydroxides of aluminum are quite frequently present in slightly acid and acid soils (Mitchell *et al.*, 1964). Bruckert (1966) and other workers reported that it is exactly under these acid conditions that the organic acids reactive towards aluminum are persistent in soils. These findings lead one to suspect that organic acids may interfere with the formation of crystalline aluminum hydroxides.

In order to ascertain the influence of the organic acids on the formation of crystalline aluminum hydroxides in the natural environment, where the concentrations of both organic acids and aluminum are low ($1{\cdot}10 \times 10^{-4}$ M and $1{\cdot}10 \times 10^{-3}$ M), $AlCl_3$ solutions containing citric acid ranging in concentration of 0, 10^{-6} and 10^{-4} M, respectively, were titrated to OH/Al molar ratio of 3·0 with 0·1 M NaOH solution. The suspensions were aged for varying periods. The precipitate was collected by ultrafiltration at a pressure of 40 psi (Huang and Luciuk, 1974). The reaction products collected were examined by X-ray powder diffraction with CuK_α radiation and replica electron microscopy. Citric acid, a strong chelating acid commonly occuring in soils, natural waters, and biological systems was chosen to reflect the similar behaviour towards aluminum of other low molecular weight organic acids common in natural systems.

Examination of the aluminum hydroxides formed at various aging periods leads to the conclusion that both the level of citric acid and the initial concentration of aluminum influence the formation of crystalline aluminum hydroxides in the system. The hydroxides formed in the absence of citric acid are essentially well crystallized bayerite at the end of a 40-day aging period (Fig. 1A). The hydroxides formed from the solution containing 10^{-3} M Al in the presence of 10^{-6} M citric acid are initially amorphous to X-rays but with time crystallinity develops. As shown in Fig. 1B, with a hydroxide aged for 40 days, well-defined peaks of gibbsite are visible on the X-ray diffraction pattern. Since an acid environment favors the crystallization of aluminum hydroxide into gibbsite relative to bayerite (Barnhisel and Rich, 1965), the acidity of citric acid apparently has helped to promote the formation of

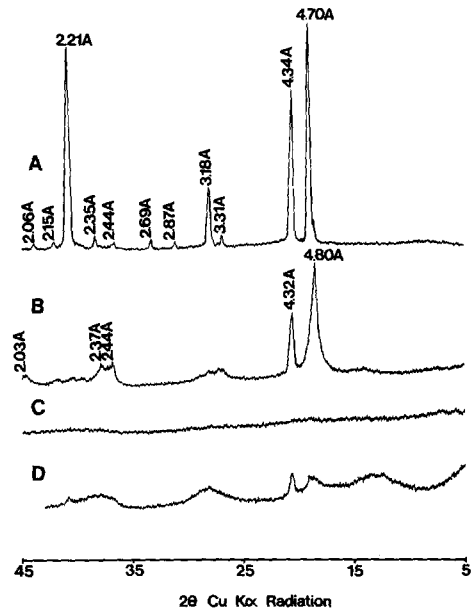

Fig. 1. X-ray diffraction patterns of hydrolytic reaction products of Al at the initial OH/Al molar ratio of 3 and (A) Al concentration of $1{\cdot}10 \times 10^{-3}$M in the absence of citric acid collected after 40 day ageing at room temperature, (B) Al concentration of $1{\cdot}10 \times 10^{-3}$ M in the presence of 10^{-6} M citric acid collected after 40 day ageing at room temperature, (C) Al concentration of $1{\cdot}10 \times 10^{-3}$ M in the presence of 10^{-4} M citric acid collected after 40 day ageing at room temperature followed by 3 day ageing at 80°C and (D) Al concentration of $1{\cdot}10 \times 10^{-4}$ M in the presence of 10^{-6} M citric acid collected after 40 day ageing at room temperature.