

ORIGIN AND POSITION OF EXCHANGE SITES IN KAOLINITE: AN ESR STUDY

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Abstract—Electron spin resonance (ESR) spectroscopy is used to investigate the nature of exchange sites on kaolinite. ESR spectra of exchangeable Cu^{2+} and Mn^{2+} on kaolinite indicate that divalent exchange ions are about 11–12Å apart on kaolinite surfaces and that planar $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ions are oriented parallel to the surfaces. Solution-like spectra for exchangeable Cu^{2+} and Mn^{2+} are observed at high relative humidities, suggesting a high degree of mobility of exchange cations on kaolinite surfaces. The evidence seems to eliminate edge sites as being active in cation exchange at least in the acidic range of pH. Similar conclusions are derived from ESR studies of Cu^{2+} -saturated talc and pyrophyllite. It is proposed that most exchange sites arise from ionic substitutions or mineral impurities in phyllosilicates.

INTRODUCTION

The source of cation exchange sites in kaolinite has never been clearly demonstrated despite the general assumption that negative charges arise from broken bonds on the edges of kaolinite plates. Thus, Grim (1968) has concluded that broken bonds are probably the major cause of exchange capacity in kaolinite minerals. In contrast, van Olphen (1966) has suggested that exchangeable cations are located on the planar surfaces of kaolinite plates and compensate a net negative charge due to a small degree of isomorphous substitution. He argued against the presence of cation exchange sites on broken edges of plates, and suggested that the edges are actually positively charged over much of the pH range. Sumner (1963) supported the concept of a net permanent charge due to isomorphous replacement in the structure, but Bundy *et al.* (1965) indicated that the presence of small amounts of smectite in kaolinite could account for the exchange capacity. Weaver and Pollard (1973) have reviewed much of the literature regarding the composition of various kaolinites, and it is apparent from this summary that there is no clear agreement as to the origin or position of exchange sites in kaolinite.

This study attempts to elucidate the properties of the exchange sites of kaolinite by the method of electron spin resonance spectroscopy (ESR). The technique has been applied previously to smectites saturated with paramagnetic ions, allowing considerable detail regarding the nature of exchange sites of layer silicates to be learned (Clementz *et al.*, 1973; McBride and Mortland, 1974; McBride *et al.*, 1975).

METHODS

Two kaolinite samples from Georgia were used in the study, kaolinite No. 4 from the American Petro-

leum Institute (A.P.I.) project No. 49 and a well crystallized Clay Minerals Source Reference sample. Both were saturated with Cu^{2+} and Mn^{2+} by washing several times in aqueous solutions of the appropriate chloride salts. The clays were then washed in distilled water until the AgNO_3 test indicated that excess chloride had been removed. Cation exchange capacities (CEC) were determined by exchanging the Mn^{2+} and Cu^{2+} ions from known quantities of these kaolinites with aqueous 0.5 N HCl and measuring Mn^{2+} and Cu^{2+} contents by atomic absorption. In addition, the kaolinite No. 4 was exchanged with Na^+ and Mg^{2+} and the cation exchange capacity for these two forms was measured by similar methods. All CEC values are averages of duplicate analyses. The pH values of the supernatants for washed Na^+ - and Mg^{2+} -saturated suspensions were 6.0–6.5 and 4.3–5.3, respectively.

The kaolinite samples were dried on glass slides and analyzed by X-ray powder diffraction in an attempt to detect mineral impurities. Oriented "discs" of kaolinite were prepared by initially drying kaolinite suspensions on a smooth surface and compressing several layers of these fragile "films" together in a Carver press for several minutes. The "discs" so produced were split into narrow strips that could be inserted in quartz tubes and oriented in the magnetic field, H , of a Varian E-12 electron spin resonance spectrometer by the method of Clementz *et al.* (1973). In addition, ESR powder spectra were obtained on kaolinites after equilibrating the samples in quartz tubes at various relative humidities (controlled by saturated salt solutions) for about one week.

DISCUSSION OF RESULTS

The CEC values for the Cu^{2+} -, Mn^{2+} -, Mg^{2+} - and Na^+ -exchanged forms of the A.P.I. kaolinite No. 4 were 13.0, 13.1, 11.1, and 7.7 m-equiv./100 g, respectively. The values for the Cu^{2+} - and Mn^{2+} -exchanged

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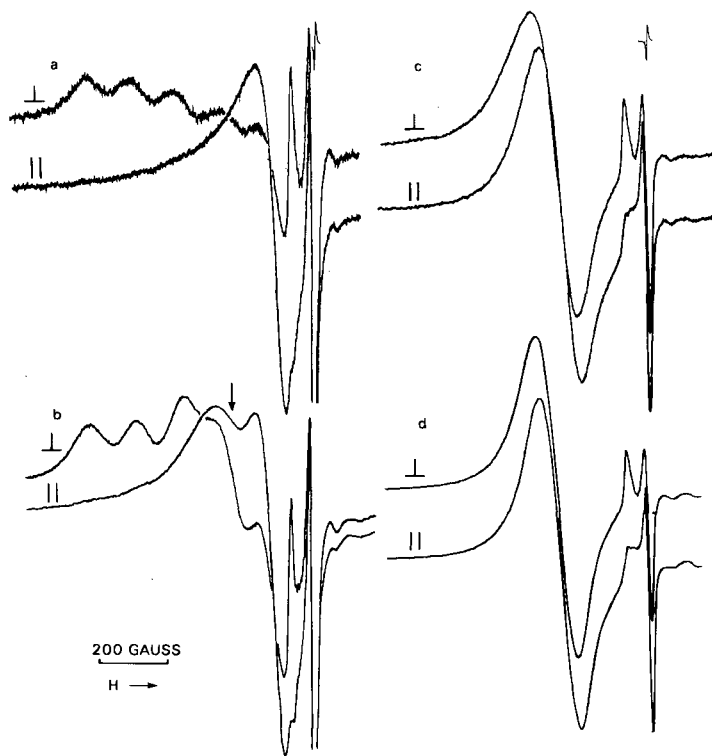


Fig. 1. ESR spectra of oriented samples of Cu^{2+} -saturated kaolinite (A.P.I. No. 4, CEC \approx 13 m-equiv./100 g) under various conditions of hydration: (a) over P_2O_5 (b) at 33% r.h. (c) at 75% r.h. (d) at 100% r.h. The symbols \parallel and \perp denote the orientation of the ab plane of the kaolinite plates relative to the magnetic field, H . The free electron position ($g = 2.0023$) is indicated by weak resonances at the top of the figure.

forms of the well-crystallized reference kaolinite sample were 1.6 and 1.2 m-equiv., respectively. In addition, X-ray powder diffraction of the kaolinites indicated that the sample with high CEC contained impurities of smectite while the low-CEC kaolinite contained no detectable impurities. It is likely, as suggested by Bundy *et al.* (1965), that the relatively high CEC is due to the presence of small amounts of smectite.

The ESR spectra of oriented films of the "high-charge" Cu^{2+} -saturated kaolinite under various conditions of hydration are shown in Fig. 1. This clay contained enough smectite impurities that it was not necessary to compress air-dried films in order to produce self-supporting, oriented samples. The typical anisotropic ESR spectrum of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ions oriented with z -axis normal to the silicate plates (Clementz *et al.*, 1973) is apparent for the kaolinite sample dried over P_2O_5 , with $g_{\parallel} = 2.338$, $g_{\perp} = 2.08$ and $A/c = 0.143 \text{ cm}^{-1}$. Two sharp resonance peaks, one near the free electron position ($g = 2.002$) and one near $g = 2.05$ originate from structure defects in the kaolinites and are described by Jones *et al.* (1974) as the g_{\perp} and g_{\parallel} values of the defect. The $g = 2.05$ resonance is not observed for the \parallel orientation of the kaolinites (Fig. 1), a result discussed by Jones *et al.* (1974). Such an anisotropic spectrum could be used as a basis for quantifying plate orientation in kaolinite samples.

The anisotropic Cu^{2+} resonance of the Cu^{2+} -exchanged kaolinite No. 4 (high charge) observed at 33% r.h. (relative humidity) indicates that much of the Cu^{2+} is oriented on the surfaces of the clay as $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ (Fig. 1b), but an isotropic resonance at $g = 2.165$ (indicated by arrow) suggests that a fraction of the Cu^{2+} is tumbling near the surfaces as $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ (Clementz *et al.*, 1973). The tumbling or dynamic Jahn-Teller distortion averages g_{\parallel} and g_{\perp} to give $g_0 = 1/3 g_{\parallel} + 2/3 g_{\perp} = 2.165$. When the r.h. is raised to 75 or 100%, virtually all the adsorbed Cu^{2+} tumbles freely as fully hydrated ions so that isotropic ESR spectra result (Fig. 1c, d). The peak to peak line width of these isotropic spectra reflects the extent of exchange narrowing, and can be used to estimate average Cu^{2+} - Cu^{2+} interionic distances (Nicula *et al.*, 1965). The average linewidth of the isotropic spectrum at 100% r.h. is 116 G, corresponding approximately to an average 11 Å Cu^{2+} - Cu^{2+} interionic separation. This is near the expected interionic distance for smectites calculated from CEC values and surface areas (McBride *et al.*, 1975). It is likely that most of the Cu^{2+} is situated on exchange sites of the smectite impurity. The Mn^{2+} -saturated form of the "high-charge" kaolinite, when equilibrated at 100% r.h., demonstrated a Mn^{2+} ESR spectrum (not shown) that indicated an average Mn^{2+} - Mn^{2+} separation of ~ 10 Å. This result was calculated from increased line widths of the Mn^{2+} spectrum due to

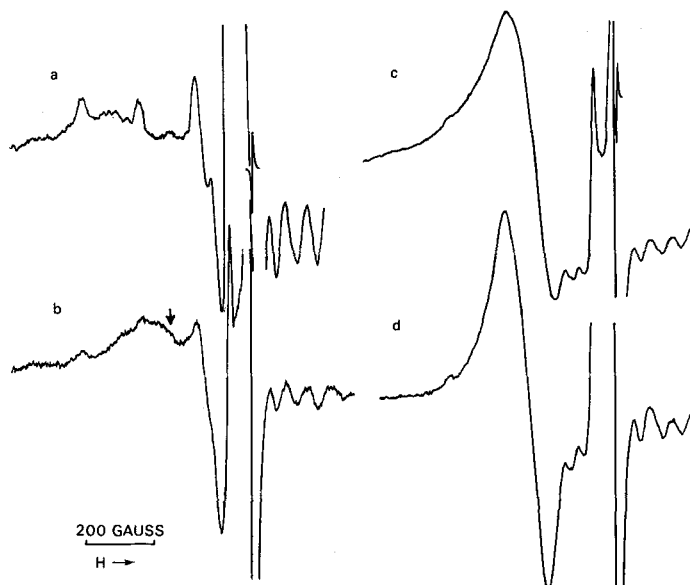


Fig. 2. Powder ESR spectra of Cu^{2+} -saturated kaolinite (Source Reference mineral, GEC \approx 1.2 m-equiv./100 g) under various conditions of hydration: (a) over P_2O_5 (b) at 33% r.h. (c) at 75% r.h. (d) at 100% r.h.

dipolar interactions of the Mn^{2+} ($S = 5/2$) ions (McBride *et al.*, 1975).

According to the direct relationship established by Van der Marel (1958) between CEC and surface areas of kaolinites, the "high-charge" kaolinite should have a surface area of about $50 \text{ m}^2/\text{g}$. With CEC of 13 m-equiv./100 g, the kaolinite should then demonstrate an average Cu^{2+} - Cu^{2+} or Mn^{2+} - Mn^{2+} separation of $\sim 11 \text{ \AA}$, a result supported by the ESR spectra. By establishing an *average* interionic distance, the ESR spectra indicate that Mn^{2+} and Cu^{2+} are *not* concentrated on edges of plates but are distributed fairly evenly over the entire surface area of the clay. It is likely that essentially all of the CEC for this "high-charge" kaolinite is due to the smectite impurity detected by X-ray powder diffraction. A small percentage of smectite in the clay could contribute a greater amount of surface area and CEC than the kaolinite itself.

The essentially pure reference kaolinite sample with very low CEC (1.2–1.6 m-equiv./100 g) was studied by the same ESR techniques as described above for the impure kaolinite. However, compression of the mineral in a press was necessary to allow samples to be manipulated. Compression also produces good orientation in clay samples that fail to dry from suspension into well-oriented films (Clementz *et al.*, 1974).

The powder spectra of Fig. 2 indicate the nature of the Cu^{2+} -kaolinite interaction under various conditions of hydration. After equilibration over P_2O_5 , the Cu^{2+} ESR spectrum is difficult to observe because of the defect spectrum of kaolinite, but is definitely anisotropic as $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ions are motionally restricted on kaolinite surfaces (Fig. 2a). At 33% r.h., there

is evidence of a weak isotropic ($g = 2.17$) resonance produced by tumbling or Jahn-Teller distortion of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ion (Fig. 2b), but most of the Cu^{2+} remains restricted on the surfaces. This signal at $g = 2.17$ is similar to the one observed on the "high charge" kaolinite at 33% r.h. (Fig. 1b), but is much weaker as a result of the lower CEC of the pure kaolinite. At higher relative humidities (75 and 100%), essentially all of the Cu^{2+} exists as rapidly tumbling $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ as the isotropic ($g = 2.17$) resonance dominates the spectra (Fig. 2c, d). The peak to peak line width of the isotropic resonance at 100% r.h. is 124 G, suggesting an average Cu^{2+} - Cu^{2+} interionic separation of 11–12 \AA . If exchangeable Cu^{2+} had been concentrated on edge sites of the kaolinite, the separation distance would have been shorter and exchange narrowing would have produced a narrower isotropic resonance (Nicula *et al.*, 1965).

The anisotropic behavior of the Cu^{2+} ESR spectrum is demonstrated in Fig. 3, where compressed oriented samples of the "low-charge" kaolinite were positioned in the magnetic field, H , of the spectrometer with the kaolinite plates parallel (\parallel) and perpendicular (\perp) to H . The spectrum of the natural kaolinite with no Cu^{2+} on exchange sites is shown in Fig. 3a. Numerous hyperfine lines are observed, possibly arising from overlap of the unpaired spin density of the structural defect with ^{27}Al and ^{25}Mg nuclei. Saturation of the exchange sites with Cu^{2+} and equilibration of the kaolinite over P_2O_5 produces an anisotropic spectrum for Cu^{2+} superimposed on the defect spectrum of kaolinite (Fig. 3b). The vertical lines denote the positions of the four hyperfine components of g_{\parallel} and the arrow indicates the position of g_{\perp} . Since

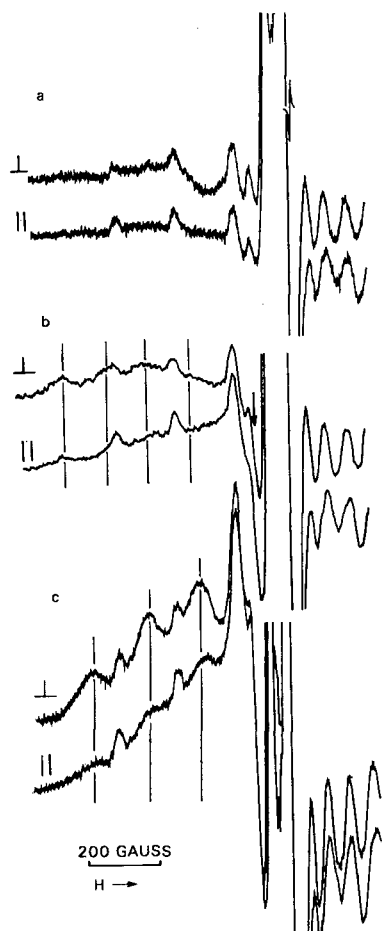


Fig. 3. ESR spectra of oriented (compressed) kaolinite (Source Reference mineral, CEC \approx 1.2 m-equiv./100 g) (a) natural (b) saturated with Cu^{2+} , dehydrated over P_2O_5 (c) saturated with Cu^{2+} , equilibrated over pyridine vapour.

the g_{\parallel} components are most intense for the \perp orientation, while g_{\perp} is strongest for the \parallel orientation, it can be concluded that the ligand z -axis of Cu^{2+} is oriented normal to the kaolinite plates (Clementz *et al.*, 1973). Probably, Cu^{2+} exists as the planar $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ion on the aluminosilicate surfaces.

A similar orientation of Cu^{2+} is observed when the Cu^{2+} -kaolinite is exposed to pyridine vapor (Fig. 3c). The planar Cu^{2+} -pyridine complex tends to lie flat on the external planar surfaces of kaolinite, an orientation that has been reported for the interlamellar regions of montmorillonite (Berkheiser and Mortland, 1975). Three of the four hyperfine components of g_{\parallel} are positioned at the vertical lines (Fig. 3c) but the fourth is obscured by the defect spectrum. The low value of g_{\parallel} (\sim 2.27) is evidence for the covalent nature of the Cu^{2+} -pyridine complex.

The orientation effects for Cu^{2+} complexes are strong evidence that essentially all of the exchange sites are on planar surfaces rather than edges of kaolinite at pH values below 7. Such orientations would not be expected for complexes adsorbed at edge sites. A similar conclusion regarding the lack of evidence

for edge sites has been made for reduced-charge montmorillonite, where $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ was found to be oriented on the clay plates (Clementz *et al.*, 1974).

Saturation of the "low-charge" kaolinite with Mn^{2+} allows the ESR spectrum of exchangeable Mn^{2+} to be recorded (Fig. 4). Normally, a six-line spectrum is observed due to coupling of the $S = 5/2$ electron spin with the $I = 5/2$ nuclear spin. Several of these lines are partially or fully obscured by the defect spectrum of the kaolinite. At 33% r.h., the spectrum is weakened and broadened by relaxation processes described elsewhere (McBride *et al.*, 1975), but the hyperfine lines remain visible (Fig. 4a). The dry kaolinite permits the $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ ions to maintain a rather low mobility, thereby resulting in line broadening. In contrast, the kaolinite at 100% r.h. has an intense, fairly narrow Mn^{2+} spectrum, suggesting much higher mobility of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$. In addition, by calculating the spectral line widths at 100% r.h. by the method of McBride *et al.* (1975), a Mn^{2+} - Mn^{2+} interionic distance of \sim 12 Å is calculated. From Van der Marel's (1958) relationship of surface area to CEC, a CEC of 1.2 m-equiv./100 g indicates a surface area of \sim 5 m²/g. The \sim 12 Å interionic distance observed for Mn^{2+} ions on kaolinite agrees with this estimate of surface area if it is assumed that the exchange ions are evenly distributed over the kaolinite surfaces.

Further evidence for cation exchange sites on the planar surfaces rather than edges of sheet silicates is provided by ESR spectra (not shown) of Cu^{2+} -saturated, oriented talc and pyrophyllite. Orientation of powdered samples was achieved by compression, and the anisotropy of the defect spectrum in both sheet

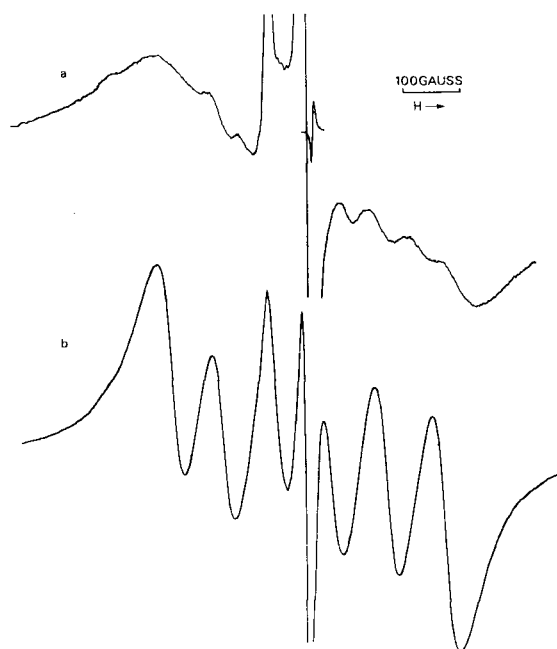


Fig. 4. Powder ESR spectra of Mn^{2+} -saturated kaolinite (Source Reference mineral, CEC \approx 1.2 m-equiv./100 g) (a) at 33% r.h. (b) at 100% r.h.

silicates (as described previously for kaolinite) indicated a high degree of orientation of the mineral particles. The similarity of the defect spectra ($g_{\perp} = 2.002$, $g_{\parallel} = 2.05$) for kaolinite, pyrophyllite, and talc indicate a common origin and suggest an electron "hole" located in a Si-O bond oriented perpendicular to the ab plane of kaolinite as proposed by Jones *et al.* (1974). The defect is stabilized by ionic substitution adjacent to the Si-O bond that produces a charge imbalance in the mineral structure. The exchangeable Cu^{2+} is oriented on air-dry talc and pyrophyllite as on kaolinite (as shown by orientation-dependent ESR spectra), again indicating adsorption on planar surfaces rather than edges. The CEC of these minerals is very low, and the Cu^{2+} spectra are rather weak. When the pyrophyllite is ball-milled (32 hr), the orientation effect is eliminated for both the Cu^{2+} and the defect spectra as the particle size is reduced to the extent that compression of the powder produces no detectable orientation of particles.

CONCLUSIONS

The concept of cation exchange sites on edges of phyllosilicate plates must be considered to be invalid at least in the acidic range of pH. ESR evidence points to the relatively even distribution of exchange sites over the planar surfaces of the silicate, indicating an average distance between divalent exchange ions of 11–12 Å. Recent ESR studies of the defect spectrum of kaolinite suggest that there is Mg^{2+} for Al^{3+} substitution in the mineral which stabilizes an electron "hole" in the structure (Jones *et al.*, 1974). This same substitution could produce a small CEC, assuming that defects are not stable near the external surfaces of kaolinite particles.

Kaolinites with relatively high exchange capacities may contain impurities of montmorillonite which account for most of the exchange sites. It is likely that very pure kaolinites have quite low CEC values (~1 m-equiv./100 g). Although it is difficult to prove that impurities do not account for the CEC of low-charge kaolinites, the Cu^{2+} ESR spectra of Cu^{2+} -saturated talc and pyrophyllite suggest that exchange sites arise from small quantities of ionic substitution in the pure minerals.

The Mn^{2+} and Cu^{2+} ions exchanged on kaolinites

as hydrated complexes demonstrate solution-like mobility at relative humidities between 75 and 100%. Although there is some evidence of rapid tumbling of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ at 33% r.h., most of it exists as planar $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ aligned with the planar surfaces of kaolinite. The evidence suggests a relatively weak, non-specific interaction between the transition metals (Cu^{2+} , Mn^{2+}) and the kaolinite surface.

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