

## HYDROLYSIS AND DEHYDRATION REACTIONS OF EXCHANGEABLE $\text{Cu}^{2+}$ ON HECTORITE<sup>1</sup>

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**Abstract**—Electron spin resonance (ESR) analysis of  $\text{Cu}^{2+}$ -hectorite suspensions provides evidence for the surface-induced hydrolysis of  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  at low pH and surface-inhibited hydrolysis (or precipitation) at high pH. Dehydration of the hectorite by heating to 110°C appears to promote hydrolysis in high pH clays further. Heating to even higher temperatures removes ligand water from  $\text{Cu}^{2+}$ , allowing the metal ion to coordinate with silicate oxygen atoms. The planar  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  ion predominates in the interlamellar regions of hectorite that has been air dried or heated to temperatures of 110°C or lower, but more extreme thermal treatment changes the apparent orientation of the  $\text{Cu}^{2+}$ -ligand axes as some or all of the four water ligands are removed. A loss in ESR signal intensity upon heating  $\text{Cu}^{2+}$ -hectorite above 110°C is evidence for lowered symmetry of the dehydrated, surface-coordinated  $\text{Cu}^{2+}$  ion.

**Key Words**—Copper, Dehydration, Electron spin resonance, Hectorite, Hydrolysis, Water.

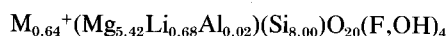
### INTRODUCTION

The ability of clay mineral surfaces to promote the hydrolysis of adsorbed metal ions has been suggested by numerous studies (Turner and Brydon, 1965; Farrah and Pickering, 1976a, 1976b; Bloom *et al.*, 1977). The evidence for surface hydrolysis is an observed release of protons into solution upon metal adsorption. However, because numerous potential sources of protons exist in an aqueous clay system (McBride, 1978), a more direct method of observing metal hydrolysis would be desirable.

Because  $\text{Cu}^{2+}$  is a  $d^9$  transition metal ion, it displays an electron spin resonance (ESR) spectrum that permits its behavior on clay surfaces to be investigated *in situ* (Clementz *et al.*, 1973; McBride *et al.*, 1975). The sensitivity of the ESR spectrum of  $\text{Cu}^{2+}$  to changes in ligand field symmetry might allow a distinction to be made between hydrolyzed and hydrated  $\text{Cu}^{2+}$ . The present study uses the ESR technique to detect changes in the nature of surface-adsorbed  $\text{Cu}^{2+}$  as a function of pH and dehydration.

### MATERIALS AND METHODS

A natural hectorite obtained from the Baroid Division of NL Industries (cation-exchange capacity = 77 meq/100 g) with structural formula:



was used. The hectorite was washed once with 0.1 N HCl to acidify it and to remove carbonate impurities, then several times with 0.1 M  $\text{CuCl}_2$ . Repeated water washing of the clay with removal of supernatant by centrifuging between washes was then carried out. The pH and  $\text{pCu}^{2+}$  of the supernatant was determined after each

wash using a glass and specific ion electrode. The washing procedure allowed a range of pH values to be attained in the clay-water system as the pH increased after each wash. Wet hectorite samples were removed and placed in capillary tubes for ESR analysis after certain pH values had been reached. Because the sample size varied from one analysis to the next, ESR signal intensities could be compared only semiquantitatively. To attain pH values above 5.5, small quantities of 0.1 N NaOH had to be added to the system. The pH was adjusted as high as 8.6, at which point the clay (which had been essentially white at lower pH) showed a distinct greenish color.

In a more quantitative experiment to evaluate  $\text{Cu}^{2+}$  ESR signal-loss as a function of pH, similarly prepared  $\text{Cu}^{2+}$ -hectorite (pH = 4.0–4.5) was doped with small amounts of a nonadsorbing nitroxide spin probe (2,2,6,6-tetramethyl-4-piperidone-1-oxyl) before pH adjustment, and then reacted with small amounts of NaOH to increase the pH. ESR spectra of these pH-adjusted samples, as well as the centrifuged clays described above, were obtained on a Varian E-104 (X-band) spectrometer at room temperature after placing the wet samples in capillary tubes. Relative ESR signal intensity of the isotropic  $\text{Cu}^{2+}$  resonance (attributable to  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ) was measured approximately for the centrifuged  $\text{Cu}^{2+}$ -hectorite as the amplitude of the signal. However, the relative  $\text{Cu}^{2+}$  signal intensity as a function of pH in the nitroxide-doped  $\text{Cu}^{2+}$ -hectorites was determined more exactly from the ratio of  $\text{Cu}^{2+}$  to nitroxide spin-probe signal intensities. Oriented clay films, obtained by drying the suspensions on a flat surface, were also analyzed by ESR in the air-dry state and after various heat treatments in quartz tubes. Rehydration of heated samples was prevented by sealing the tubes with parafilm. The films were aligned perpendic-

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ular ( $\perp$ ) and parallel ( $\parallel$ ) to the magnetic field,  $H$ , of the spectrometer.

To determine the  $\text{Cu}^{2+}$  content of the  $\text{Cu}^{2+}$ -saturated hectorite (after several washings with distilled water had increased the supernatant pH to 4.6), the clay was titrated with NaOH, and the endpoint was determined by a rapid pH increase. The results showed that at a pH of 7.7 essentially all of the  $\text{Cu}^{2+}$  had been hydrolyzed and that 103 meq  $\text{Cu}^{2+}/100$  g was present in the clay. This high value may be due to the removal of impurities such as calcite during the acid wash of hectorite as well as the tendency of divalent ions to give higher estimates of the CEC than monovalent ions.

The quantity of adsorbed water on  $\text{Cu}^{2+}$ -hectorite at several temperatures was determined by heating air-dry clay to 110°, 170°, and 350°C for 1 hr and recording the weight loss. The number of water molecules per  $\text{Cu}^{2+}$  ion was determined by assuming that all adsorbed water had been driven off at 350°C.

## RESULTS AND DISCUSSION

Eight samples of the repeatedly washed hectorite were taken for study, based upon the pH values of their equilibrium supernatants. These were numbered 1 through 8 for reference purposes, and the properties of their supernatants are shown in Table 1. The  $\text{pCu}^{2+} + 2\text{pOH}$  value of 18.56 for sample 8 indicates that the solubility product of  $\text{Cu}(\text{OH})_2$  had been exceeded, accounting for the greenish color of this sample. However, all other systems were undersaturated with respect to  $\text{Cu}(\text{OH})_2$ , which has a  $\text{pK}_{\text{SO}} = 19.36$  (Baes and Mesmer, 1976).

The ESR spectra of the wet hectorite samples (Figure 1) were essentially symmetrical single resonances with  $g = 2.19$  and peak to peak linewidths of 130–140 gauss, evidence of  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  undergoing rapid tumbling or Jahn-Teller distortion (Clementz *et al.*, 1973). Upward adjustment of the pH produced a definite decrease in signal intensity for similar quantities of sample, as shown by the spectra of Figure 1. The relative peak heights (determined with an accuracy of about  $\pm 25\%$ ) are plotted in Figure 2, and compared with the fraction of soluble copper (in the absence of clay) that remains as  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  with changing pH as calculated from known stability constants of  $\text{CuOH}^+$ ,  $\text{Cu}_2(\text{OH})_2^{2+}$ , and  $\text{CuCO}_3^0$  (Baes and Mesmer, 1976). The decrease in signal intensity is almost certainly associated with an hydrolysis or complexation reaction of  $\text{Cu}^{2+}$  on the clay surface, reducing the concentration of  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ . The complex must have either no ESR signal, or one that is broadened beyond detection, because no new signal appeared at the expense of the isotropic resonance. The dominant hydrolysis product of  $\text{Cu}^{2+}$  in concentrated solution is  $\text{Cu}_2(\text{OH})_2^{2+}$  (Baes and Mesmer, 1976). Although this is not necessarily the dominant species formed in the interlayer positions of clays, the concen-

trated interlamellar "solution" of  $\text{Cu}^{2+}$  might favor its formation over monomers such as  $\text{CuOH}^+$ . Spin pairing in  $\text{Cu}_2(\text{OH})_2^{2+}$  could possibly cause a loss of paramagnetism, a phenomenon that may also reduce ESR signal intensity of  $\text{Cu}^{2+}$  in Y zeolites (Conesa and Soria, 1978a). The observation that ions such as  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  do not form similar dimers upon hydrolysis (Baes and Mesmer, 1976) suggests that electron pairing stabilizes the  $\text{Cu}_2(\text{OH})_2^{2+}$  species because of the  $d^9$  electron configuration of  $\text{Cu}^{2+}$ . It is also possible that  $\text{CuOH}^+$ , with a reduced ligand symmetry relative to the axially symmetrical  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  has a very broad resonance not detectable by ESR. Similarly,  $\text{CuCO}_3^0$  in solution appears to give no ESR signal because of its low symmetry or low concentration, while the planar  $\text{Cu}(\text{OH})_4^{2-}$  ion which forms in aqueous solutions at very high pH produces an isotropic four-line resonance.

Regardless of the product formed on the clay, surface hydrolysis (or complexation) is evident at higher pH as indicated by loss in signal intensity (Figure 2). Calculations based upon the formation constants of  $\text{Cu}_2(\text{OH})_2^{2+}$  and  $\text{CuOH}^+$  (Baes and Mesmer, 1976) indicate that less than 3% of solution copper in equilibrium with the  $\text{Cu}^{2+}$ -hectorite (Table 1) was in the  $\text{CuOH}^+$  form at a pH of 6.5 and that  $\text{Cu}_2(\text{OH})_2^{2+}$  was insignificant. At pH 7, less than 10% of the copper in solution could have been  $\text{CuOH}^+$  and no significant amount of  $\text{Cu}_2(\text{OH})_2^{2+}$  was present. However, at pH 7.75 and higher, most of the soluble copper in equilibrium with the clay should have been in the form of  $\text{CuCO}_3^0$ . Therefore, the decrease in ESR signal intensity of the hectorite suspensions at low pH values which do not allow significant solution hydrolysis or complexation of copper is probably associated with surface-enhanced hydrolysis. It is possible that nucleation of  $\text{Cu}(\text{OH})_2$  on the silicate surface occurs in much the same way that aluminum hydroxide is adsorbed on clays (Turner and Brydon, 1965) with an apparent solubility product considerably lower than that of the hydroxide precipitated in solution. The data of Table 1 indicate that the apparent solubility product remains below the level of the least soluble Cu precipitates, tenorite and malachite, for the first 7 samples.

At pH values above 7, the expected fraction of solution Cu in the  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  form decreased rapidly as a result of the formation of  $\text{CuOH}^+$  and  $\text{CuCO}_3^0$ . At pH 8 and above most of the soluble Cu is in the neutral  $\text{CuCO}_3^0$  form as calculated from known stability constants and assuming equilibrium of the clay suspension with atmospheric  $\text{CO}_2$ . Thus, a comparison of the fraction of Cu as  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  in the solution phase and clay phase suggests that, at lower pH surface adsorption enhances  $\text{Cu}^{2+}$  hydrolysis, while at higher pH the reverse effect occurs (Figure 2). Such an observation would be expected if the surface promoted the formation of a polymer with the formula  $\text{Cu}(\text{OH})_x^{(2-x)+}$  where

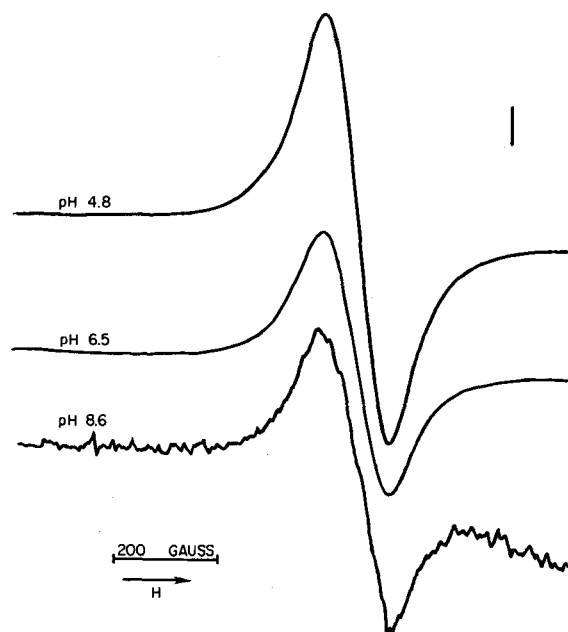


Figure 1. ESR spectra of wet suspensions of  $\text{Cu}^{2+}$ -hectorite after adjustment to pH values of 4.8 (sample 2), 6.5 (sample 5), and 8.6 (sample 8). The instrument gain used for sample 8 was four times greater than for samples 2 and 5. (The vertical marker indicates the  $g = 2.0027$  field position.)

$x < 2$ . The pH-pCu solubility line for this surface-nucleated species would have a slope of  $x$ . Compared to  $\text{Cu}(\text{OH})_2$  with slope 2, this adsorbed species could then have a lower solubility than  $\text{Cu}(\text{OH})_2$  at low pH and a higher solubility than  $\text{Cu}(\text{OH})_2$  at high pH, accounting for the behavior of the ESR signal intensity.

A more quantitative ESR study of this phenomenon using nitroxide as an internal standard shows the effect of the clay surface on  $\text{Cu}^{2+}$  complexation even more clearly. While the ESR signal of 0.01 M  $\text{CuCl}_2$  decreases abruptly above pH 5 as  $\text{Cu}(\text{OH})_2$  precipitates, the signal of exchangeable  $\text{Cu}^{2+}$  on hectorite decreases more gradually (Figure 3). The result again points to the ability of the surface to promote  $\text{Cu}^{2+}$  hydrolysis at low pH and inhibit (or delay) hydrolysis at high pH. The latter effect may be largely a kinetic phenomenon, because a study of  $\text{Cu}^{2+}$ -hectorites initially adjusted to pH values greater than 5 showed a slow downward drift in pH for several days until they equilibrated near the  $\text{Cu}(\text{OH})_2$  titration curve (Figure 3). It is likely that the adsorbed  $\text{Cu}^{2+}$  was partially protected from hydrolysis in interlamellar positions, but was slowly released to hydrolyze and possibly nucleate on surfaces.

After the clay suspensions were air-dried to form oriented films, the ESR spectra (Figure 4) indicated the alignment of  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  ions in the interlamellar regions of the hectorite (Clementz *et al.*, 1973). The parameters obtained from these spectra are  $g_{\perp} = 2.073$ ,

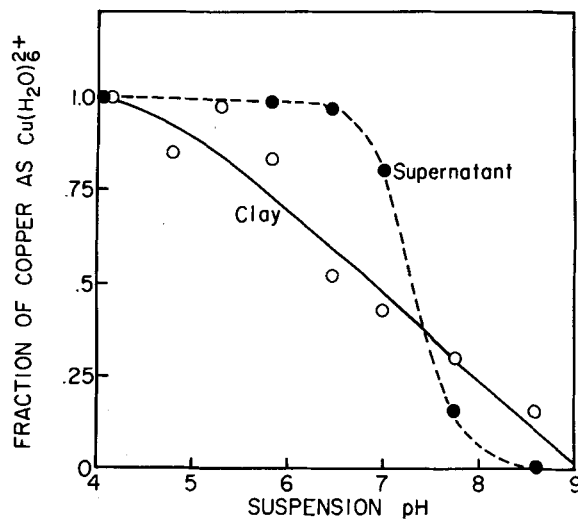


Figure 2. The effect of suspension pH upon the fraction of adsorbed Cu present as  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ , as determined from the intensity of the isotropic ESR signal in  $\text{Cu}^{2+}$ -hectorite. For comparison, the fraction of soluble  $\text{Cu}^{2+}$  present in the supernatant as  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  is calculated from the data of Table 1 and the known stability constants of Cu-hydroxy and carbonate complexes.

$g_{\parallel} = 2.347$ , and a hyperfine splitting ( $A/c$ ) of  $0.0163 \text{ cm}^{-1}$ . A signal attributable to tumbling or distorting  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  was also observed when the clays were at ambient conditions, with an averaged  $g$ -value of 2.164 (position denoted by arrow in Figure 4). This signal was largely obscured by the highest field hyperfine component of  $g_{\parallel}$  when the clay film was oriented perpendicular to the magnetic field, but was quite visible for the parallel orientation. The intensity of the  $g_{\perp}$  and  $g_{\parallel}$  spectral components was much reduced at high pH (Figure 4), indicating that a portion of the  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  ions converted to a hydrolyzed form at higher pH. The upward adjustment of pH had no significant effect on the ESR parameters, suggesting that none of the hydrolysis products of  $\text{Cu}^{2+}$  (e.g.,  $\text{CuOH}^+$ ,  $\text{Cu}_2(\text{OH})_2^{2+}$ ) were observable by ESR.

Table 1. Properties of the supernatants in equilibrium with  $\text{Cu}^{2+}$ -hectorite gels.

Sample no.	pH	pCu	pCu + 2pOH
1	4.13	2.55	22.29
2	4.78	4.49	22.93
3	5.28	5.44	22.88
4	5.83	5.87	22.21
5	6.46	6.63	21.71
6	6.98	6.80	20.84
7	7.74	7.49	20.01
8	8.58	7.72	18.56

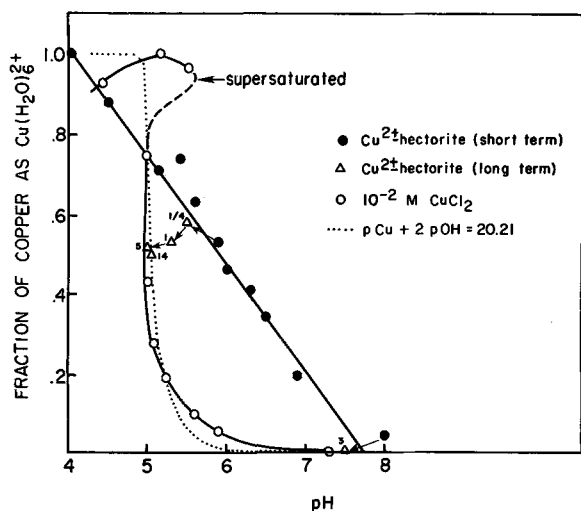


Figure 3. The effect of pH on the fraction of Cu present as  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  in pure solution (0.01 M  $\text{CuCl}_2$ ) and  $\text{Cu}^{2+}$ -hectorite as determined by the intensity of the isotropic ESR signal and internal spin standard. For comparison, a theoretical line (dotted) is plotted assuming the precipitation of a  $\text{Cu}(\text{OH})_2$  phase with solubility given by  $\text{pCu} + 2\text{pOH} = 20.21$ . The effect of time on the  $\text{Cu}^{2+}$ -hectorite data is denoted by open triangles accompanied by numbers indicating the number of days of reaction time.

Further removal of water from the clay by heating produced more changes in the ESR spectra. After heating the clay at  $110^\circ\text{C}$  for 1 hr, the  $g = 2.164$  signal disappeared, signifying complete conversion of any  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  ions to  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  (Figure 5a). In addition, significant shifts in the spectral parameters occurred ( $g_{\parallel} = 2.37$ ,  $g_{\perp} = 2.08$ ,  $A/c = 0.0158 \text{ cm}^{-1}$ ). The value of  $g_{\parallel}$  is considered the most sensitive indicator of covalency, and an increase in  $g_{\parallel}$  accompanied by a decrease in  $A/c$  is evidence of a decrease in the covalent nature of the  $\text{Cu}^{2+}$ -ligand bonds (Kivelson and Neiman, 1961). However, calculation of  $\alpha^2$ , a parameter indicating the degree of  $\text{Cu}-\text{O}$   $\sigma$ -bond covalency, produces values of 0.87 for both the air-dried and heated clays. Thus, the  $\sigma$ -bonds are quite ionic in nature and unaffected by heating. The effect of heating on ESR parameters may arise from distortion of the square planar symmetry accompanying partial collapse of interlayers. Previous studies (McBride and Mortland, 1974) showed that  $\text{Cu}^{2+}$ -smectites collapse from 12.4 to 11.7 Å upon heating to  $100^\circ\text{C}$ , indicating partial removal of the monolayer of interlamellar water and possible distortion of the planar  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  ion.

More extreme heating at  $170^\circ\text{C}$  and  $205^\circ\text{C}$  greatly reduced the apparent intensity of the  $g_{\parallel}$  component, whereas the  $g_{\perp}$  resonance remained distinct (Figure 5b, 5c). The loss of  $g_{\parallel}$  signal intensity is probably associated with the further removal of  $\text{H}_2\text{O}$  from  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ , thereby allowing direct silicate oxygen- $\text{Cu}^{2+}$  contact.

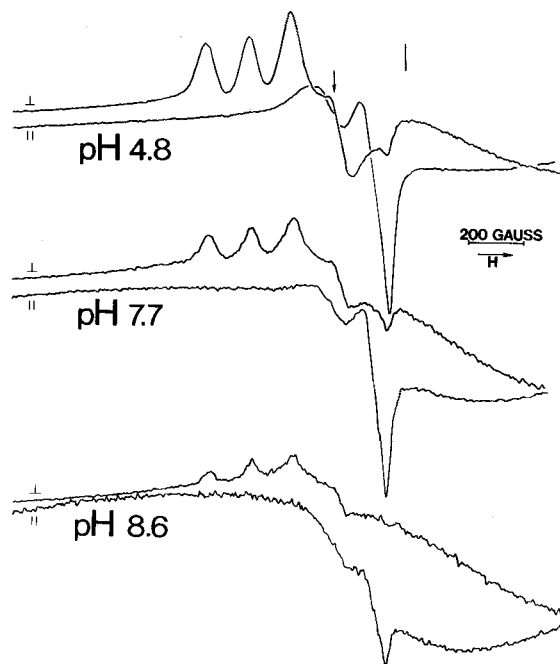


Figure 4. ESR spectra of air-dry  $\text{Cu}^{2+}$ -hectorite films oriented perpendicular ( $\perp$ ) and parallel ( $\parallel$ ) to the magnetic field direction. Films used were prepared from suspensions of hectorite samples 2 (pH = 4.8), 7 (pH = 7.7), and 8 (pH = 8.6).

This result is consistent with the observed collapse of  $\text{Cu}^{2+}$ -smectite basal spacings to 9.7 Å upon heating at  $150^\circ\text{C}$  or higher (McBride and Mortland, 1974). Similar heating studies of  $\text{Cu}^{2+}$  in zeolites have shown maximum ESR signal loss in the  $100^\circ\text{C}$ - $120^\circ\text{C}$  range, suggesting lowered symmetry as the  $\text{Cu}^{2+}$  ion coordinates to surface oxygens (Conesa and Soria, 1978b). In addition, hydrolysis reactions of  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  are likely to occur in the heated clays as the remaining ligand water is strongly polarized by  $\text{Cu}^{2+}$ . The resulting surface-coordinated and hydrolyzed species with lower symmetry than square planar, may have a range of  $g_{\parallel}$  and  $A/c$  values which greatly broadens the observed spectral components of  $g_{\parallel}$ . Because  $g_{\perp}$  is much less sensitive to changes in ligand symmetry or covalency, and the hyperfine splitting of the  $g_{\perp}$  resonance is small, much less broadening of the  $g_{\perp}$  signal should occur as verified by the strong  $g_{\perp}$  resonance of Figure 5b and 5c.

After  $170^\circ\text{C}$  heating, the weak  $g_{\parallel}$  hyperfine lines were observed for both orientations of the clay films relative to the magnetic field (Figure 5b). This is an indication of the loss of orientation of  $\text{Cu}^{2+}$  as a square planar complex aligned with the clay surface, resulting from the complete interlamellar collapse at temperatures above  $150^\circ\text{C}$  (McBride and Mortland, 1974). After  $205^\circ\text{C}$  heating, there is evidence that the parallel orientation of the clay produced the most distinct  $g_{\parallel}$  components (Figure

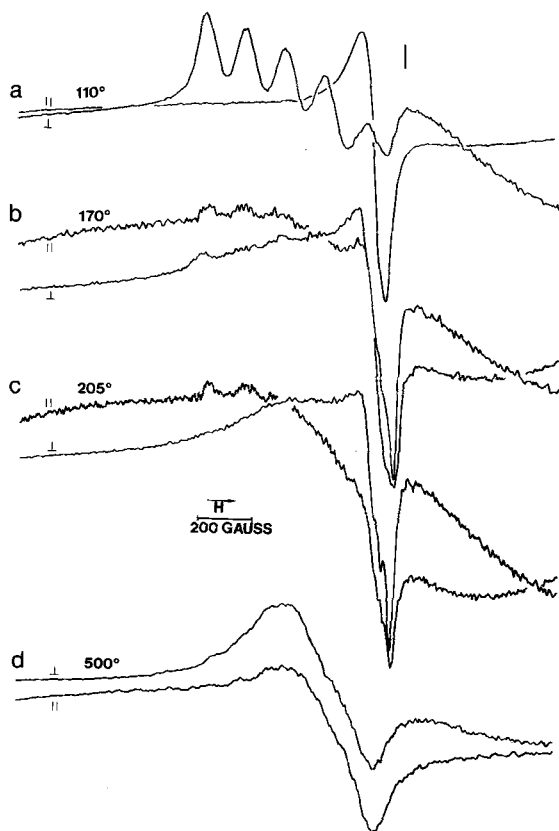


Figure 5. ESR spectra of  $\text{Cu}^{2+}$ -hectorite films oriented perpendicular ( $\perp$ ) and parallel ( $\parallel$ ) to the magnetic field direction after heat treatment for 1 hr at 110°, 170°, 205°, and 500°C.

5c), a reversal of the results for the air-dry or 110°C heated clay. This change may mean that the last water molecules associated with  $\text{Cu}^{2+}$  were driven off, and the  $\text{Cu}^{2+}$  coordinated in such a way with surface oxygens to change the symmetry axis orientation relative to the clay platelets. Upon heating to very high temperatures (500°C), the loss of resolution of hyperfine structure as well as the lack of orientation compared to the lower temperatures (Figure 5d) suggests that the  $\text{Cu}^{2+}$  entered sites of poorly defined symmetry.

The process of water removal at 110°C does not greatly reduce the intensity of the ESR spectrum of  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  in the acidified clays. For example, the spectrum of sample 3 heated to 110°C was almost as intense and distinct as the spectrum of the air-dried

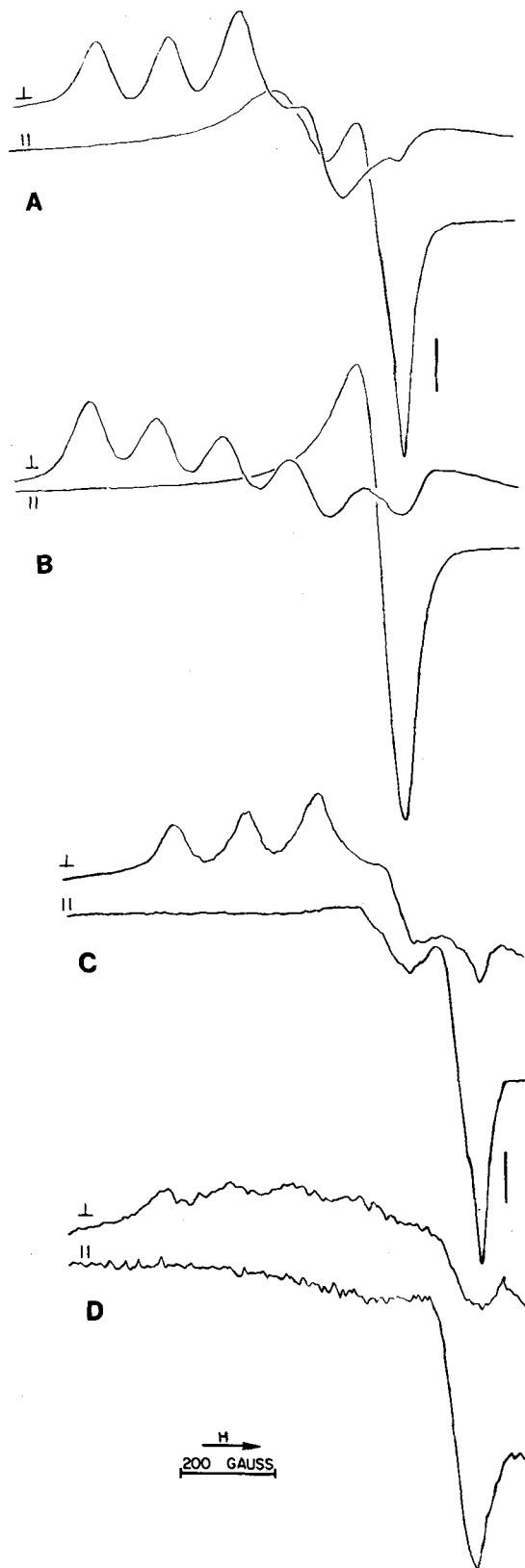


Figure 6. ESR spectra of  $\text{Cu}^{2+}$ -hectorite films oriented perpendicular ( $\perp$ ) and parallel ( $\parallel$ ) to the magnetic field direction. The spectra shown are for sample 3 (pH = 5.3) air-dried (A) and heated to 110°C (B), and for sample 7 (pH = 7.7) air-dried (C) and heated to 110°C (D). Instrument gains were  $2.5 \times 10^2$  (A),  $4 \times 10^2$  (B),  $2.5 \times 10^2$  (C),  $6.3 \times 10^2$  (D).

sample (Figure 6a). In contrast, the higher pH clays demonstrated very indistinct spectra upon drying at  $110^\circ\text{C}$ , as shown by sample 7 (Figure 6c). It is likely that the drying process promotes hydrolysis of  $\text{Cu}^{2+}$  to hydroxy-Cu species, especially when the pH is initially high. Studies of the acidity of clay surfaces as a function of hydration have shown that the removal of water generates protons by metal ion hydrolysis (Mortland and Raman, 1968).

In summary, the clay surface affects  $\text{Cu}^{2+}$  hydrolysis reactions. Whereas a hectorite suspension enhances  $\text{Cu}^{2+}$  hydrolysis at low pH by the preferential adsorption of hydrolysis products, the clay inhibits or at least delays Cu-hydroxy or Cu-carbonate complex formation at high pH.

Removal of adsorbed water by heating the air-dry  $\text{Cu}^{2+}$ -hectorite to  $110^\circ\text{C}$  eliminates all remaining  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  species which may have been present on external surfaces and internal "micropores" created by the irregular stacking of clay platelets. The planar  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  ion is formed by the removal of axial water and becomes highly oriented between clay platelets. Drying at  $110^\circ\text{C}$  also appears to promote hydrolysis of  $\text{Cu}^{2+}$ , at least in clays initially adjusted to higher pH. Temperatures of  $170^\circ\text{C}$  and higher remove some of the ligand water of  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ , thereby forcing  $\text{Cu}^{2+}$  to coordinate with silicate oxygens as the interlamellar spacing collapses. These conclusions from ESR data are consistent with thermogravimetric data which indicate that 17–18, 4–5, and 2–3 water molecules are associated with each adsorbed  $\text{Cu}^{2+}$  ion in hectorite that has been air-dried, heated to  $110^\circ\text{C}$ , and heated to  $170^\circ\text{C}$ , respectively.

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**Резюме**—Посредством электронного спинового резонанса (ЭСР) суспензий  $\text{Cu}^{2+}$ -гекторит получено доказательство для существования поверхностно-индуцированного гидролиза  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  при низких pH и поверхностно-ингибиторного гидролиза (или осаждения) при высоких pH. Дегидратация гекторита при нагреве до  $110^\circ\text{C}$  приводит к активации гидролиза в глинах с высоким pH, дальнейший обогрев до высоких температур удаляет лиганд воды из  $\text{Cu}^{2+}$ , позволяя иону металла координировать с атомами кислорода силиката. Плоскостный ион  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  преобладает в межламельных зонах гекторита, который сушился на воздухе либо обогревался до  $110^\circ\text{C}$  или низшей температуры. Более предельная сверхтермическая обработка изменяет кажущуюся ориентацию осей лиганда  $\text{Cu}^{2+}$  по мере того как некоторые либо все из четырех лигандов воды удалены. Потеря интенсивности сигнала ЭСР при обогреве  $\text{Cu}^{2+}$ -гекторита свыше  $110^\circ\text{C}$  является доказательством для обнижения симметрии дегидратированного поверхностно-координированного иона  $\text{Cu}^{2+}$ . [E.C.]

**Resümee**—Die Electronenspinresonanz-Analyse (ESR) von  $\text{Cu}^{2+}$ -Hektorit-suspensionen zeigen, daß eine durch die Oberfläche geförderte Hydrolyse von  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  bei niedrigen pH-Werten und eine durch die Oberfläche verhinderte Hydrolyse (oder Ausfällung) bei hohen pH-Werten stattfindet. Die Dehydratation des Hektorit durch Erhitzen auf  $110^\circ\text{C}$  scheint die Hydrolyse in Tonen mit hohem pH weiter zu fördern. Beim Erhitzen auf noch höhere Temperaturen wird das Ligandenwasser von  $\text{Cu}^{2+}$  entfernt, wodurch sich das Metallion mit Silikatsauerstoffatomen koordinieren kann. Das planare  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ -Ion ist in den interlamellaren Bereichen von Hektorit, der Luft getrocknet oder bis maximal  $110^\circ\text{C}$  erhitzt wurde, vorherrschend. Eine Erhitzung auf höhere Temperaturen verändert jedoch die Orientierung der  $\text{Cu}^{2+}$ -Ligandenachsen, da einige oder alle der vier Wasserliganden entfernt werden. Eine Verminderung der ESR-Signalintensität nach dem Erhitzen von  $\text{Cu}^{2+}$ -Hektorit über  $110^\circ\text{C}$  zeigt die Symmetrieverringung der dehydratisierten Oberflächen-koordinierten  $\text{Cu}^{2+}$ -Ionen. [U.W.]

**Résumé**—L'analyse par resonance à spin d'électrons de suspensions d'hectorite- $\text{Cu}^{2+}$  fournit l'évidence pour l'hydrolyse induite à la surface de  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  à un pH bas, et pour l'hydrolyse inhibée à la surface (ou pour la précipitation) à un pH élevé. La déshydratation de l'hectorite par échauffement à  $110^\circ\text{C}$  semble d'avantage promouvoir l'hydrolyse dans des argiles à pH élevé. L'échauffement à des températures encore plus élevées enlève l'eau ligande de  $\text{Cu}^{2+}$ , permettant une coordination de l'ion métal avec des atomes oxygènes silicates. L'ion  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  plane domine dans les régions interfolaires de l'hectorite séchée à l'air ou échauffée à  $110^\circ\text{C}$  ou à des températures plus basses, mais un traitement thermal plus extrême change l'orientation apparente des axes ligands  $\text{Cu}^{2+}$  puisque certains ou tous les quatre ligands aqueux sont retirés. Une perte d'intensité du signal ESR lorsque l'hectorite est chauffée au delà de  $110^\circ\text{C}$  est une preuve de la symétrie amoindrie de l'ion  $\text{Cu}^{2+}$  déshydraté coordonné à la surface. [D.J.]