

## MIGRATION OF Cu IONS IN Cu MONTMORILLONITE HEATED WITH AND WITHOUT ALKALI HALIDES

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**Abstract**—Cu montmorillonite heated with or without potassium halide was studied by IR and ESR spectroscopy, supplemented by XRD measurements, microprobe and chemical analyses. It appears that on heating Cu montmorillonite, most of the Cu ions migrate into hexagonal cavities and eventually, when dehydroxylation occurs, into octahedral vacancies. Some Cu ions may penetrate into octahedral vacancies before dehydroxylation. In the presence of potassium halide, deprotonation facilitates penetration of Cu into octahedral vacancies. The presence within the layers of non-exchangeable Cu ions that are inaccessible to water does not necessarily cause the perturbation of OH bending vibrations conventionally attributed to migration of small cations into the structure. Such perturbation was only observed when the basal spacing was reduced to  $\sim 9.5\text{\AA}$ .

**Key Words**—Cu-montmorillonite, K-halide, IR and ESR spectra.

### INTRODUCTION

When dioctahedral smectites with small interlayer cations are heated to 200–300°C, some of these ions become non-exchangeable, provided that the clay has an octahedral charge deficit. Numerous investigators debated the question of the location of these “fixed” ions—hexagonal cavities versus octahedral vacancies. The earlier work was well summarized by Brindley and Lemaire (1987). Following White *et al* (1961), Calvet and Prost (1971) and McBride and Mortland (1974) perturbation of the OH bands in infra-red spectra have been regarded as criteria for the migration of small interlayer cations into the layer structure. Recently Srassra *et al* (1994) showed that the bands corresponding to OH bending vibrations of heated Li-montmorillonite can be resolved into components corresponding to the original vibrations and those due to OH associations of Li in the octahedral sheets.

In the course of a study of montmorillonites heated with alkali halides, which act as proton acceptors and ion exchangers, it was found that, although small interlayer cations became largely non-exchangeable after heating, the OH regions of most of the infra-red spectra were not perturbed (Heller-Kallai 1975a). This suggests that factors other than the position of the small compensating cations may contribute to the perturbation of OH vibrations of heated montmorillonites. The present investigation was undertaken to test this hypothesis and, if possible, to establish the path followed by small cations penetrating into the layer structure. Cu<sup>2+</sup> montmorillonite was chosen for the purpose, because the environment of the Cu<sup>2+</sup> ions could be monitored by electron spin resonance. Heated Cu-montmorillonite was previously studied by McBride and Mortland (1974), but the present investigation was ex-

tended to include alkali halide treated as well as partially dehydroxylated samples.

### EXPERIMENTAL

The samples studied were either the same or similar to those previously prepared for use as solid phases in liquid chromatography (Tsvetkov *et al* 1993). Briefly, Cu<sup>2+</sup> saturated Wyoming montmorillonite was heated alone or in the presence of KBr or KCl in the ratio 1:7 at 550°C for various periods of time. Excess alkali halide was removed by washing. Aliquots of the samples were spray-dried (SP) at inlet/outlet temperatures of 350–360/110°C. In addition, a sample of the original montmorillonite was potassium halide treated, subsequently saturated with Cu and spray-dried. The samples used and the nomenclature adopted, which follows Tsvetkov *et al* (1993), are presented in Table 1.

XRD patterns of air-dried and glycolated samples, IR spectra and chemical analyses were obtained as described by Tsvetkov *et al* (1993).

ESR spectra were recorded at 293K with an X-band Brücker ER 200 spectrometer, using randomly oriented powders in an air-dried and water-soaked condition (Mosser *et al* 1990). Dry samples were inserted into quartz tubes and samples that were soaked in water for 48 hours were measured in a flat glass cell.

### RESULTS AND INTERPRETATION

Pertinent results are summarized in Table 1. Selected IR spectra are shown in Figure 1 and ESR spectra in Figure 2.

#### *M-Cu and heated M-Cu*

The Cu-saturated sample had a d-spacing of 12.4Å in the air-dried state, expanded on glycolation and

Table 1. Nomenclature and selected characteristics of the samples.

Sample*	Cations		XRD (Å)		IR (cm <sup>-1</sup> )		ESR (g)		I**
	Cu meq/100 g	K	Air dried	Glyco- lated	Si-O	OH stretch.	OH bending	Dry	
M-Cu	100		12.4	17.0	1049	3631	917, 880, 847	2.04	2.15
SP (M-Cu)	100	5	9.4	9.4	1068-1044	3654, 3644	936, 876	2.06	2.06, 211
(M-Cu) <sup>5</sup>	100	5	9.4, 9.54	9.4, 9.54	1072-1052	v.w.	936, 876	2.06	2.06
M-Cu-KBr <sup>1</sup>	88	46	11.9	17.0	1047	3635	918, 879, 850	2.04	2.05
SP (M-Cu-KBr) <sup>1</sup>	88	46	11.95	16.7	1038	3643-3629	918, 879, 850	2.04	2.05
M-Cu-KBr <sup>5</sup>	88	146	12.3	13.4	1035	3633	916, 881, 850	2.04	2.04
SP (M-Cu-KBr) <sup>5</sup>	88	146	12.3	16.7, 13.6	1035	3633	916, 881, 850	2.05	2.05
SP (M-KCl) <sup>5</sup> -Cu	120	13	9.55	17, 9.6	1067-1039	3644	932, 875	2.05	2.05

\* M-Cu: copper-saturated montmorillonite; KBr (KCl): potassium halide treated; Superscript: hours of heating at 550°C; SP: spray-dried.

\*\* I: Intensity Cu (g ~ 2)/Fe (g ~ 4).

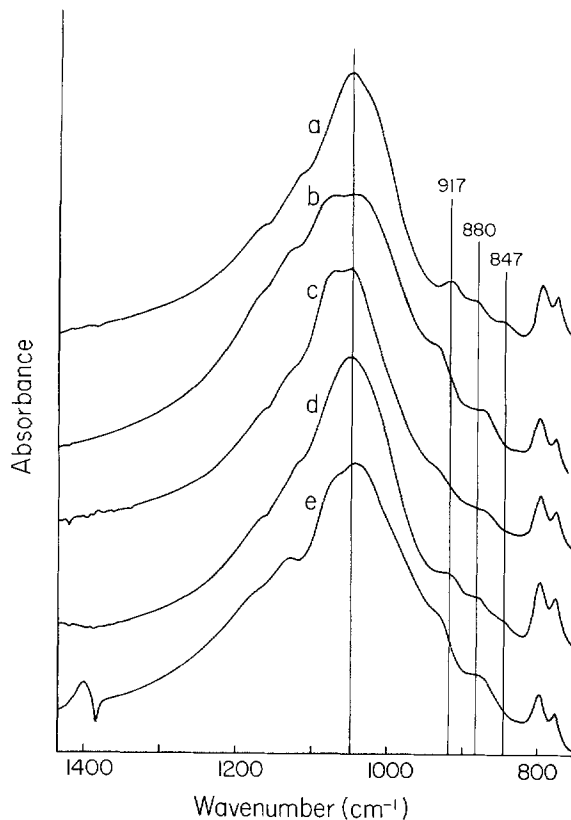


Figure 1. Infrared spectrum of a) Cu montmorillonite (M-Cu); b) Spray dried Cu montmorillonite [SP(M-Cu)]; c) Cu montmorillonite heated 5 hours at 550°C [(M-Cu)<sup>5</sup>]; d) Cu montmorillonite treated with KBr for 1 hour (M-Cu-KBr<sup>1</sup>); e) Montmorillonite treated with KCl for 5 hours, exchanged with Cu and spray dried [SP(M-KCl)<sup>5</sup>-Cu].

showed the usual IR spectrum of Wyoming montmorillonite (Figure 1a). Following Farmer (1974), the bands at 917, 880, and 847 cm<sup>-1</sup> are assigned to Al-OH-Al, Al-OH-Fe, and Al-OH-Mg bending vibrations respectively. The sample contained 100 meq Cu/100g clay (heated at 550°C), which exceeds the CEC of Wyoming montmorillonite and probably indicates that some hydrolysis had occurred. A shift in the resonance from an anisotropic  $g = 2.04$  to an isotropic  $g = 2.15$  signal in the ESR spectrum of the dry sample toward an isotropic  $g = 2.15$  signal in that of the water-soaked sample demonstrates that the Cu ions were readily accessible to water (Table 1 and Figure 2).

After spray-drying, which involved heating to about 350°C, the sample SP(M-Cu) collapsed to 9.4 Å and did not expand on glycolation (Table 1). The IR spectrum shows the perturbed OH bending modes at 936 and 876 cm<sup>-1</sup> conventionally regarded as characteristic of heated montmorillonites saturated with small cations (Figure 1b). No unperturbed Al-OH-Al or Al-OH-Mg vibrations persisted at this stage. The OH stretching

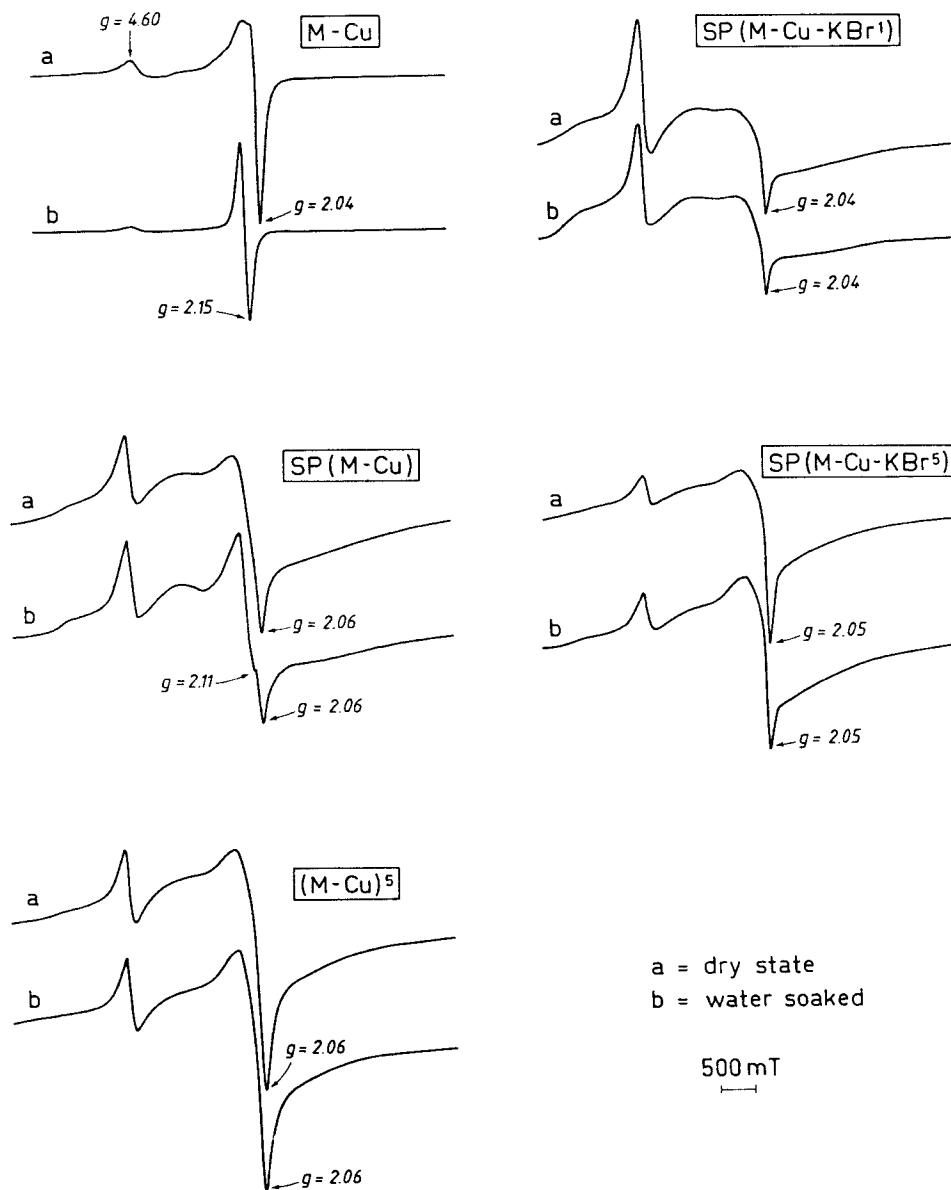


Figure 2. ESR spectra of dry and water-soaked samples. Nomenclature as in Figure 1.

vibrations were also shifted and the main Si-O vibration at  $1049\text{ cm}^{-1}$  was broadened and partly shifted toward a higher frequency. ESR spectra demonstrated that although most of the Cu was inaccessible to water, some Cu ions remained free to tumble ( $g = 2.06$  and  $2.11$  respectively, Figure 2). Comparison of the intensity of the Cu signal with that of iron present in the structure,  $\text{Cu}(g \sim 2)/\text{Fe}(g \sim 4)$  (Table 1), shows that there was considerable loss of Cu signal intensity, as previously observed by McBride and Mortland (1974) for Cu montmorillonite heated up to  $270^\circ\text{C}$ . This in-

dicates a change in the environment of the Cu ions either due to bonding, which would effectively reduce the charge, or to relaxation effects. McBride and Mortland (1974) observed that unheated Cu-montmorillonite and the sample heated for 24 hours at  $200^\circ\text{C}$  had similar magnetic susceptibilities and therefore concluded that no electron pairing (bonding) occurred under these experimental conditions.

After heating Cu montmorillonite to  $550^\circ\text{C}$  for 5 hours,  $(\text{M-Cu})^5$ , a mixture of two components was obtained with basal spacings of  $9.40$  and  $9.54\text{ \AA}$ , which

were determined from higher order reflections. Both components were nonexpanding with glycol. The intensity of the OH bands in the IR spectrum was greatly reduced, but their frequencies remained the same as after heating to 350°C. The main Si-O absorption became narrower and clearly exhibits two maxima (Table 1 and Figure 1c). Changes in lattice vibrations in the 470–530  $\text{cm}^{-1}$  region confirmed that some structural changes had occurred, but this spectral region was not studied in detail. ESR spectra show an anisotropic feature with partially regained Cu signal intensity and a  $g$ -value of 2.06, which remained unchanged in the wet sample (Table 1 and Figure 2).

Although these data do not permit an unequivocal assessment of the position of the Cu ions, it seems reasonable to infer that, on heating to 350°C, most of them migrated into hexagonal holes. McBride and Mortland (1974) concluded that up to 30% of Cu ions penetrated into octahedral vacancies below 270°C. The collapsed interlayers prevented access of water to all the Cu ions, except those which remained exposed on external surfaces. After heating to 550°C, the sample was partly dehydroxylated, as witnessed by the increased basal spacing, the reduced intensity of the OH vibrations and changes in lattice modes. ESR spectra showed that all the Cu ions were inaccessible to water. Probably dehydroxylation facilitated penetration of all the Cu ions into the octahedral sheets. If Cu ions were situated in hexagonal cavities, it would be expected that on outer surfaces some would be accessible to water, as was observed after milder heating. Dehydroxylation generally commences on outer surfaces, where water molecules can easily diffuse outwards. This explains why no Cu ions remained free to tumble after only partial dehydroxylation of the sample. The increase in signal intensity of the ESR spectrum, even if small, confirms that a rise in temperature from 350° to 550°C caused changes in the environment of the Cu ions.

#### *M-Cu-KBr<sup>1</sup> and M-Cu-KBr<sup>5</sup>*

After heating with potassium halide for one hour (M-Cu-KBr<sup>1</sup>), most of the Cu present in the initial sample persisted in the structure while K was taken up (Table 1). This was previously observed with Mg saturated samples and was attributed to deprotonation of structural OH groups (Heller-Kallai 1975a, 1975b). The observation that Cu was not displaced by K on heating with excess K halide followed by exhaustive washing demonstrates that it is non-exchangeable. The basal spacing, which was 11.9Å after heating 1 hour, increased slightly with continued heat treatment. Microprobe analysis showed that, after five hours' heating, when much more K was introduced into the sample, small amounts of a separate Cu-containing phase,

probably copper oxide, developed. The intensity of the OH vibrations, both stretching and bending, was progressively reduced, as expected on deprotonation. In contrast to the samples heated without alkali halide, the frequency of the remaining OH bands remained unchanged. However, the frequency of the principal Si-O vibration was reduced. This shift is in the opposite direction from that observed with samples heated in the absence of alkali halides (Table 1 and Figure 1), indicating that the structural changes differed from those occurring on dehydroxylation (Heller-Kallai 1975a, 1975b).

ESR spectra show that the Cu ions in both samples were inaccessible to water, even though the interlayers were not collapsed (Table 1, Figure 2). Cu signal intensity was lost in the spectrum recorded after heating one hour, but was partly regained after heating five hours, much more so than with the sample heated without KBr. In fact, the increase in signal intensity per structural Cu ion in sample M-Cu-KBr<sup>5</sup> is even greater than appears from Table 1. According to the microprobe analysis, some copper was expelled from the structure in the course of heating. The ESR signal of copper oxide is a broad modulation covering nearly 1000 Tesla and does not obscure the signal due to Cu in the clay. The reduced intensity of the signal after 1 hour's heating may again be attributed to lattice relaxation effects. As more energy was provided, Cu migrated into octahedral vacancies and signal intensity was partially regained.

It seems probable that deprotonation, which occurs on heating with alkali halides, facilitates penetration of Cu ions into the hexagonal cavities or the octahedral sheets. The ESR spectra indicate that the latter is more probable. Cu ions in hexagonal cavities would be partially accessible to water as was observed with sample SP(M-Cu). Wherever these Cu ions are situated, they are non-exchangeable, yet at no stage do they cause the perturbation of OH vibrations conventionally attributed to migration of small cations into the layers of dioctahedral smectites.

#### *SP(M-KCl<sup>5</sup>-Cu)*

In this sample the order of pretreatment was reversed. It was first heated with KCl, then Cu saturated and finally spray-dried. This sample contained more Cu than any of the other samples studied (Table 1), because some of the K introduced into the partially deprotonated sample was replaced by Cu. The interlayers were collapsed in the air-dried state, but were partly expanded on glycolation. The IR spectrum of this sample resembles that of sample SP(M-Cu) (Table 1 and Figure 1e). A large resonance centered at  $g = 2$  in the ESR spectrum indicates magnetic Cu-Cu interaction, probably due to inhomogeneous distribution of Cu in the sample.

## DISCUSSION

Integration of the results obtained suggests the following scenario: on spray-drying, which involved heating to 350°C, most of the Cu ions migrated into hexagonal cavities. Some of these ions may have penetrated into octahedral vacancies, as reported by McBride and Mortland (1974). On heating to higher temperatures a change in environment of the Cu ions occurred, as shown by the increased intensity of the ESR signal. Similar variations in ESR signal intensity on heating with K halides also reflect changes in position of the Cu ions. When sufficient energy was provided, dehydroxylation, which occurred if Cu-montmorillonite was heated alone, or partial deprotonation, which took place upon heating with K halides, removed the obstacle to penetration of the divalent ions into octahedral sheets. In the initial stages of migration, copper ions occupied positions close to hydroxyl groups or to oxygens of deprotonated hydroxyl groups, causing a reduction in intensity of the ESR signal. As more energy was supplied, Cu ions migrated further into the octahedral sites and some ESR signal intensity was regained. The difference in final signal intensity between the dehydroxylated and deprotonated samples is probably due to differences in coordination of the Cu ions. In the deprotonated samples, Cu ions are 6-coordinated giving rise to a more intense signal than in dehydroxylated samples where Cu ions may either occupy 5- or very distorted 6-coordinated sites (Wardle and Brindley 1972; Heller-Kallai and Rozenon 1980).

Sample M-Cu-KBr<sup>1</sup> contained 46 meq K and 88 meq Cu per 100 g clay. If each equivalent of K displaced one proton and if each proton removed facilitated entry of one Cu ion into an octahedral vacancy, all the Cu ions could be accommodated in the octahedral sheets. It appears that these ions do not cause perturbation of the OH vibrations. If the generally accepted practice of assigning OH bands to various cation-OH combinations is valid, such perturbation would at most, be very limited. New bands corresponding to various Cu-OH combinations, analogous to those observed by Srasra *et al* (1994) for Li in octahedral sheets, were not found. The ratio of divalent compensating ions to octahedral vacancies in Wyoming montmorillonite is 0.32:2 (McBride and Mortland 1974). If one OH is deprotonated for every Cu entering the octahedral sheet, the proportion of OH groups bonded to Cu is less than 10% of all the OH groups and the intensity of the bands due to each of the various combinations will be correspondingly low, even if Cu ions were confined to positions adjacent to Mg ions.

In contrast to the K halide treated samples, Cu-montmorillonite heated alone gave rise to spectra with perturbed OH bands. McBride and Mortland (1974) reported that on heating Cu montmorillonite up to 200–270°C about 30% of the Cu ions became non-

exchangeable, that is about 0.1 Cu ion for every 4 OH groups. The OH bending vibrations were perturbed. On reexpansion of the layers with water-ethanol mixtures, the original spectrum was regained except for most of the Al-OH-Mg vibrations. They attributed this to the effect of Cu ions in octahedral vacancies and differentiated between a reversible “hexagonal shift” due to Cu ions in hexagonal holes and an irreversible “octahedral shift”. In view of the small number of Cu ions in the octahedral sheets (0.1 Cu ions to 0.66 Mg ions) only a minor fraction of the Al-OH-Mg groups can be directly involved in bonding with Cu. If deformation of the entire sheet is invoked, it seems probable that all the OH vibrations would be affected, which was not observed. These observations remain unexplained. The reversible perturbation may be due to one or both of the following causes: distortion of the layers due to the presence of Cu ions in the hexagonal cavities and/or the concomitant close approach of adjacent silicate layers. Large interlayer cations cannot penetrate deeply into the hexagonal vacancies and would therefore be expected to cause less distortion of the layers and to preclude very close approach of neighboring layers. The fact that the Al-OH-Al in-plane vibrations of pyrophyllite, which has no interlayer cations, occur at 950 cm<sup>-1</sup> (Farmer 1974) supports the conjecture that the perturbation is caused by the proximity of neighboring layers. Moreover, perturbation of OH vibrations was not observed in the spectrum of any montmorillonite saturated with small cations other than Li and heated with alkali halides in this or in previous studies (Heller-Kallai 1975a, 1975b). This suggests that it is not due to the presence of small non-exchangeable cations within the layers. Migration of Cu ions into the octahedral sheets on partial dehydroxylation does not change the frequencies of the residual OH vibrations. This indicates that the perturbation is independent of the position of the Cu ions within the layers.

Small monovalent and divalent compensating ions in montmorillonite appear to behave differently on heating. Srasra *et al* (1994) demonstrated that Li enters octahedral vacancies before dehydroxylation occurs. Heller-Kallai (1975a) noted a difference between Li- and Mg-montmorillonites heated with K halides. While the spectrum of Li-montmorillonite was perturbed, that of Mg-montmorillonite, like the spectrum of Cu-montmorillonite in the present study, was not. Re-examination of the spectrum of Li-montmorillonite heated with KBr at 300°C for 1 hour (unpublished) showed that the band with a maximum at 925 cm<sup>-1</sup> is broad and probably comprises the Al-Al-OH and Al-Al-Li-OH bands at 915 and 935 cm<sup>-1</sup> respectively, that were observed by Srasra *et al* (1994). No unperturbed OH bending vibrations were detected in the spectra of heated Cu montmorillonite. It seems that monovalent Li ions readily penetrate into octahedral vacancies before dehydroxylation or deprotonation occurs, whereas most

of the divalent Cu ions, with a similar ionic radius, do not.

### CONCLUSIONS

On heating Cu montmorillonite to 350°C most of the Cu ions moved into hexagonal holes. A minor fraction may have penetrated into octahedral vacancies. On further heating, when dehydroxylation occurred the Cu ions migrated from the hexagonal holes into octahedral vacancies. On heating in the presence of alkali halides, deprotonation of OH groups freed the pathway for penetration of Cu ions into the octahedral sheets.

Perturbation of the OH bending vibrations was only observed when the basal spacing was reduced to  $\sim 9.5 \text{ \AA}$ . It appears to be independent of the position of the Cu ions within the layers. The layers of Cu montmorillonite heated with KBr were not collapsed and the OH bands were not perturbed.

Comparison with literature data on Li montmorillonite shows that although Li and Cu have similar ionic radii, the lower charge of Li facilitates penetration into the octahedral sheets, which occurs before either dehydroxylation or deprotonation.

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