

PROPERTIES OF REDUCED CHARGE MONTMORILLONITES: HYDRATED Cu(II) IONS AS A SPECTROSCOPIC PROBE*

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Abstract—A series of Cu(II) reduced charge montmorillonites (RCM) of varying charge reduction has been prepared by exchange of the parent Li(I)–Na(I) mineral with CuCl₂ in 95 per cent ethanol solution. The Cu(II) exchange capacity, as determined by Na(I) exchange in 1:1 (v/v) ethanol–water, is a linear function of the fraction of Li(I) initially present on the exchange sites, *F*. Selective Cu(II)-saturation on internal and external sites was achieved at maximum charge reduction (*F* = 1.0). Water sorption isotherms and (001) basal spacings are interpreted in terms of an increasing tendency toward interlayer collapse with increasing charge reduction. Because of the higher hydration energy of the Cu(II) ion, however, the fraction of non-expandible interlayers at a given *F* value is lower than those present in the corresponding Li(I)–Na(I) RCM. Electron spin resonance spectra of oriented samples show that under air-dried conditions (ca. 40 per cent r.h.) the predominant Cu(II) species present, whether on internal or external sites, is the planar Cu(H₂O)₄²⁺ ion. The symmetry axis of the ion is oriented perpendicular to the *a*–*b* plane of the silicate sheets. In the presence of a full partial pressure of water, the Cu(II) ions on the external sites and those which are in expandible interlayers become totally hydrated Cu(H₂O)₆²⁺ and tumble rapidly. The Cu(H₂O)₄²⁺ ions in non-expandible layers retain their restricted orientation on the silicate surface. Some general conclusions have been drawn regarding the nature of charge distribution in the mineral.

INTRODUCTION

The thermal migration of exchangeable cations, such as lithium, into vacant octahedral positions in montmorillonite has been known for nearly two decades. An important consequence of this cation migration is the reduction in the surface charge of the mineral and the concomitant increase in the mean distance between the cations remaining on the interlamellar surfaces. Variable charge reduction can be achieved by introducing along with Li(I) on the initial exchange sites an ion [e.g. Na(I)] which is too large to penetrate the silicate structure upon heat treatment. Above a critical concentration of Li(I) corresponding to ca. 50 per cent of the initial CEC, the reduced charge minerals resist reexpansion by water. However, recent studies have shown that the reduced charged minerals can be swelled by certain solvents such as ethanol, glycol and morpholine (Calvet and Prost, 1971; Brindley and Ertem, 1971; Ertem, 1972). These latter solvents should provide a means of replacing the exchangeable Li⁺ and Na⁺ ions with any desired cation.

It has been demonstrated recently that Cu(II) ions can serve as a useful probe in detecting environmental influences of silicate surfaces on exchangeable ions by electron spin resonance (e.s.r.) spectroscopy (Clementz *et al.*, 1973). The technique has been applied in the current study to obtain structural information for hydrated Cu(II) ions on the internal and external exchange sites of reduced charge montmorillonites (hereafter designated as RCM). In addition, CEC and water sorption isotherms have been determined for the Cu(II)-saturated RCM in order to assess the effect of the transition metal ion on the cation exchange and swelling properties of the mineral.

EXPERIMENTAL

Preparation of RCM

A series of RCM samples was prepared by the method of Brindley and Ertem (1971). Suspensions of <2 μm Li(I)-saturated and Na(I)-saturated Upton, Wyoming, montmorillonite (A.P.I. H-25) were mixed in various proportions and classified with regard to the fraction, *F*, of lithium ions occupying the exchange sites prior to heat treatment. The *F* values for the four

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samples in the series were 0.0 [no lithium present in the Na(I)-montmorillonite], 0.2, 0.6 and 1.0 [no sodium added to the Li(I)-montmorillonite]. The suspensions (approx. 600 ml, 0.0047 g ml^{-1}) were stirred for 24 hr to allow maximum randomization of ions and then dried into large thin films (approx. $6 \times 12 \text{ in.}$) on polyethylene sheets. These clay films were peeled from the polyethylene and heated for 24 hr at 220°C . It was believed that this technique would promote homogeneous distribution of ions in all layers.

After cooling, the clay films were suspended in 95 per cent ethanol and dispersed in a Waring blender. The ethanol suspensions were concentrated, and the clay was collected by vacuum filtration. One portion of each airdried, Li(I)-Na(I) RCM sample was saved for the water sorption study.

Cu(II) exchange forms

(a). *Cu(II) saturation of internal and external sites.* Total Cu(II) saturation was achieved for RCM at all four F values by stirring the samples for 15-hr periods in 1 N CuCl_2 /95 per cent ethanol solution and repeating the procedure two more times. Excess CuCl_2 was removed by washing with 95 per cent ethanol until a Cl^- test with AgNO_3 was negative. The samples were allowed to dry in air to remove excess ethanol and were then equilibrated at 20°C and 40 per cent r.h. for 24 hr. All of the Cu(II) ions can be exchanged off with three washes of CaCl_2 in ethanol, as verified by the loss of a Cu(II) e.s.r. signal.

(b). *Cu(II) saturation of internal sites.* X-ray diffraction experiments (see below) indicated that Cu(II)-saturated RCM with F values of 0.6 and 1.0 would undergo limited swelling upon exposure to liquid water. Thus, it was assumed that a large organic cation in aqueous solution would readily exchange Cu(II) on external sites but have difficulty in penetrating the interlamellar space to exchange internal Cu(II) ions. One-g samples of totally Cu(II)-saturated RCM with F values of 0.6 and 1.0 were quickly washed three times with 50 ml of an aqueous 0.5 N tetrabutylammonium chloride solution. The wash procedure required approximately 10 min to complete. Excess $[\text{Bu}_4\text{N}]\text{Cl}$ was removed by washing with water.

(c). *Cu(II) saturation of external sites.* One-g samples of untreated Li(I)-Na(I) RCM with F values of 0.6 and 1.0 were heated to 110°C for 1 hr to insure removal of interlamellar ethanol. Each sample was stirred three times in aqueous 1 N CuCl_2 , and then washed free of excess Cl^- with water. The samples were dried and equilibrated at 20°C and 40°C r.h. This procedure should have rendered all of the external exchange sites Cu(II)-saturated with the internal sites largely unexchanged.

I.R. studies

Thin films of the RCM samples were dried onto Irttran windows and scanned on a Beckman IR-7 spectrophotometer. Lithium migration into the structure was verified by observing the changes in the OH 'wag' vibrations in the $700\text{--}900 \text{ cm}^{-1}$ region as discussed by Calvet and Prost (1971).

Charge reduction measurements

Charge reduction in RCM was verified by determining the amount of exchangeable Cu(II) present in the totally-saturated Cu(II) exchange forms of various F values. A modification of the Mortland and Mellor (1954) technique was used which consisted of suspending the clays in a 50:50 (v/v) mixture of 95 per cent ethanol and water, and titrating conductrometrically with standard NaOH. The titration curves were linear with only one end-point.

Water sorption

The Cu(II)-saturated samples and the unexchanged RCM's were equilibrated for 1 week under 7 different partial pressures of water vapor provided by various saturated salt and sulfuric acid solutions. The weight gain with increasing partial pressure was recorded.

X-ray diffraction studies

The (001) reflections of the samples under various conditions were measured by depositing thin films of the mineral on glass slides. A Philips X-ray diffractometer with copper radiation and a nickel filter was employed.

E.S.R.

Some degree of orientation of crystallites was necessary to give detailed spectral information. Where possible, the oriented film technique employed earlier (Clementz *et al.*, 1973) was used. Samples which did not make good oriented films (e.g. $F = 1.0$) were pressed into disks (Angel and Hall, 1972) under 10,000 psi for 3 min on a Carver Press. Narrow strips were sliced from these disks for use as oriented samples. X-band spectra were recorded on a Varian E-4 spectrometer.

RESULTS AND DISCUSSION

The CEC of Cu(II)-saturated RCM, as determined by Na(I) exchange in 1:1 (v/v) ethanol-water, exhibits a linear dependence on F , the fraction Li(I) initially present on the exchange sites (see Fig. 1). At $F = 1.0$, a residual CEC of 27 m-equiv per 100 g is retained which corresponds to about twice the negative charge

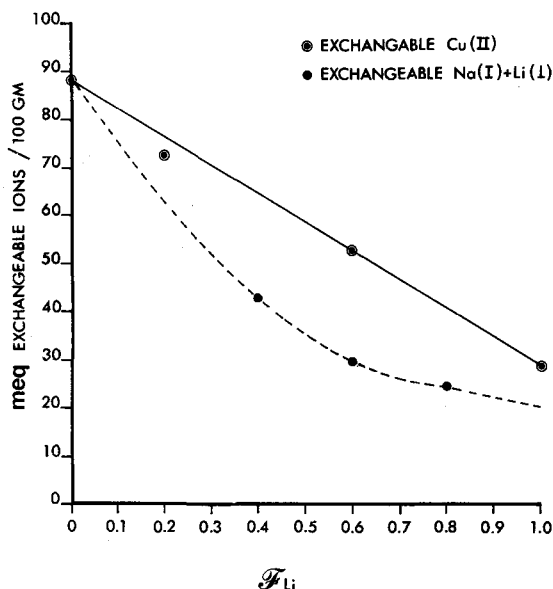


Fig. 1. Solid line, plot of m-equiv of exchangeable ions on Cu(II)-saturated RCM, as determined by Na(I) exchange in 1:1 (v/v) H₂O-ethanol, vs F , the fraction of exchangeable Li(I) in the preheated clay. Dashed line, analogous plot of exchangeable Na(I) and Li(I) in RCM as determined by Brindley and Ertem (1971).

arising from tetrahedral substitution of Al(III) for Si(IV) in the mineral (unit cell formula, $M(\text{I})_{0.64}[\text{Al}_{3.06}\text{Fe}_{0.32}\text{Mg}_{0.66}](\text{Al}_{0.10}\text{Si}_{7.9})\text{O}_{20}(\text{OH})_4$).

Included in Fig. 1 for comparison purposes are the data of Brindley and Ertem (1971) for exchange of Li(I)-Na(I) RCM in ammonium acetate solution. The non-linear dependence on F and lower CEC values relative to those obtained for Cu(II) RCM may be due in part to differences in exchange conditions. That is, Cu(II) in ethanol may be more effective than NH_4^+ in aqueous solution in replacing Li(I) and Na(I) in these reduced charge systems. The differences in the data may also arise because of differences in experimental technique. It is believed that protons are generated during the heat treatment of these clays (Farmer and Russell, 1967; Ertem, 1971). The protons could migrate to octahedral sites, satisfy charge, and limit Li(I) migration. Resolution of the RCM can cause the protons to leave the octahedral positions (Mortland, 1966), thus reinstating the negative charge on the silicate structure. Since Brindley and Ertem specifically analyzed for the Li(I) and Na(I) exchanged by NH_4^+ and CEC arising from exchangeable protons would be undetected.

Water sorption isotherms for Cu(II)-saturated and unexchanged Li(I)-Na(I) forms of RCM are shown in Fig. 2. The isotherms reveal two important effects. First, a marked reduction in sorption occurs with de-

creasing layer charge for the Cu(II)-saturated forms (Fig. 2a). Second, the presence of Cu(II) on the exchange sites increases the water sorption over that of the unexchanged Li(I)-Na(I) RCM with F values of 0.6 and 1.0 (Figs. 2b and 2c). The two effects underscore the importance of metal ion hydration in the sorption process. The enthalpy of hydration of Cu(II) is $-2100 \text{ kJ mole}^{-1}$, whereas for Li(I) and Na(I) the hydration enthalpies are -579 and $-406 \text{ kJ mole}^{-1}$, respectively (Cotton and Wilkinson, 1972).

It has been previously shown that below a 'critical CEC' corresponding to an F value of ca. 0.5, unexchanged Li(I)-Na(I) RCM resists expansion by water (Brindley and Ertem, 1971; Calvet and Prost, 1971). The low water sorption shown in Figs. 2(b) and (c) for the Li(I)-Na(I) RCM samples with F values of 0.6 and 1.0 are consistent with silicate layers being completely collapsed. In the air-dried state both of these reduced-charge forms of the mineral exhibit a broad (001) X-ray reflection centered at 10.0 \AA . Since the spacing is not altered appreciably when the minerals are exposed to a free water surface, the possibility of any substantial interlamellar water sorption is precluded. The presence of collapsed, nonexpansible interlayers also readily accounts for the virtually identical water sorption isotherm at these two F values.

In marked contrast to the Li(I)-Na(I) RCM, the corresponding Cu(II)-saturated forms with $F = 0.6$ and 1.0 exhibit appreciably different water sorption capacities (see Fig. 2a). Under air-dried conditions, the broad (001) reflections are centered at 11.6 and 10.4 \AA , respectively, for Cu(II) RCM at $F = 0.6$ and 1.0 . In comparison, air-dried Cu(II) RCM at $F = 0.0$ and 0.2 , exhibits uniform (001) spacings of 12.3 \AA . Exposure of the $F = 0.6$ sample to water vapor causes the low angle side of the (001) reflection to broaden markedly, whereas the analogous broadening at $F = 1.0$ is much less pronounced. It is concluded, therefore, that Cu(II) is more effective than Li(I)-Na(I) in promoting the expansion by water of some interlayers in an interstratified RCM at $F = 0.6$, but that at $F = 1.0$ most of the interlayers remain nonexpansible even in the presence of Cu(II).

Under air-dried conditions all of the Cu(II)-saturated RCM samples exhibit esr spectra consisting of g_{\parallel} and g_{\perp} components as expected for Cu(II) ions with axial symmetry. A typical spectrum for a randomly oriented powder sample with an F value of 0.0 is shown in Fig. 3(a). The low field resonance with $g \approx 4$ is present in the native mineral and is attributed to iron within the silicate structure (Angel and Hall, 1972). The hyperfine components of g_{\perp} are unresolved, but those of g_{\parallel} can be distinguished. Perhaps anisotropic effects contribute somewhat to line broadening (Adrian, 1968).

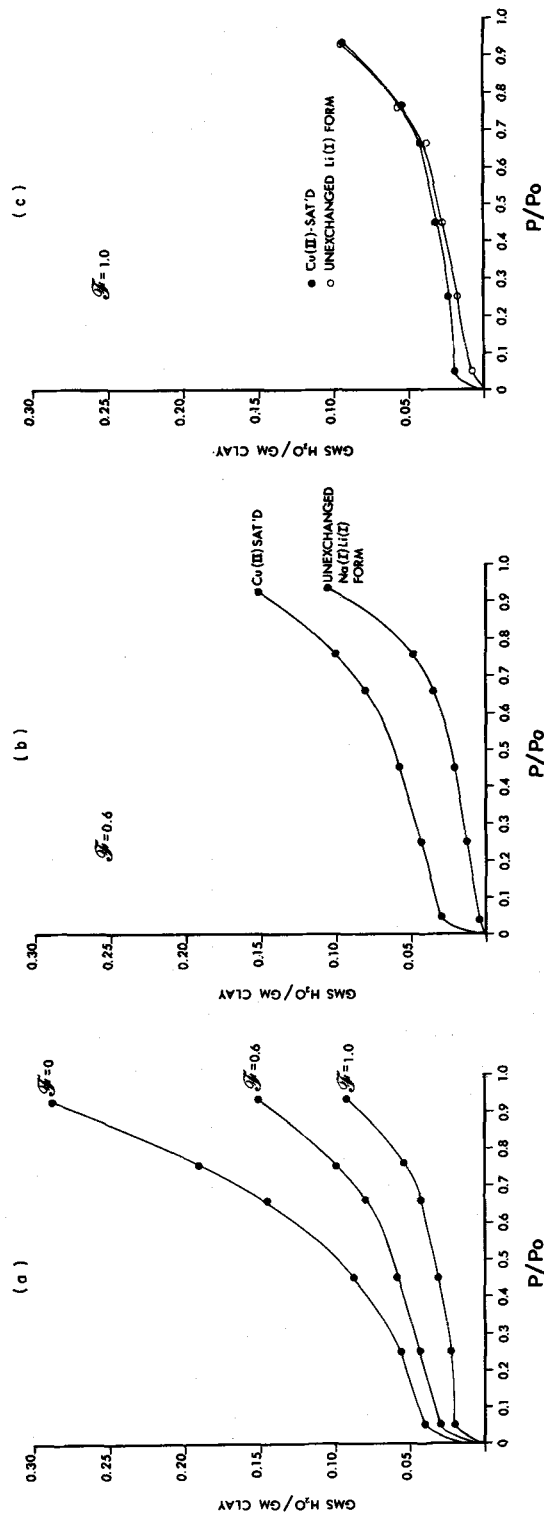


Fig. 2. Water adsorption isotherms: (a) Cu(II)-saturated RCM having varying amounts of charge reduction; (b and c) Cu(II)-exchanged forms of RCM and their unexchanged Na⁺-Li⁺ counterparts with F values of 0.6 and 1.0, respectively.

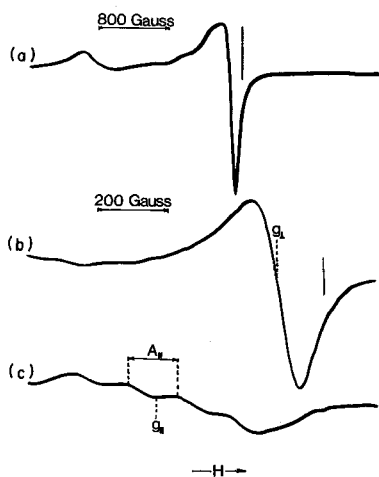


Fig. 3. E.S.R. spectra (first derivative representations) for Cu(II)-montmorillonite (RCM, $F = 0$). (a) 4000 G scan of an air-dry, randomly oriented powder sample; (b) 1000 G scan of an air-dry, oriented film sample with the a - b planes of the silicate layers positioned parallel to H ; (c) the spectrum of the same sample when the a - b planes of the silicate layers are positioned perpendicular to H . The solid vertical line indicates the resonance position of a standard strong pitch sample with $g = 2.0028$. All spectra obtained at 300°K .

When the spectrum of an oriented film is recorded with the silicate layers parallel to the direction of the magnetic field (H), only g_{\perp} is observed as shown in Fig. 3(b). Orientation of the film perpendicular to H gives rise only to the well resolved A_{\parallel} components of g_{\parallel} (Fig. 3c). Clearly, the symmetry axis of the aquated Cu(II) ion is oriented perpendicular to the silicate layers. Analogous spectral results were obtained for oriented samples of Cu(II) RCM with F values of 0.2, 0.6 and 1.0. Table 1 presents a summary of the CEC and e.s.r. data for oriented, air-dried samples of Cu(II) RCM.

Since under air-dried conditions, the (001) spacings indicate there is sufficient space in the interlayer to accommodate at best only a monolayer of water, the most reasonable formulation for the hydrated Cu(II) giving rise to the above esr spectra is $\text{Cu}(\text{H}_2\text{O})_4^{2+}$. As the interlayers begin to collapse at low charge values,

water is expelled from outer coordination spheres of the Cu(II) ion, but regardless of the extent of charge reduction, an appreciable fraction of the copper ions retain inner sphere water. Any Cu(II) devoid of coordinated water in totally collapsed interlayers would be difficult to observe by e.s.r. in the presence of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$. For example, an internally Cu(II)-saturated RCM sample which was heated at 200°C for 1 hr to drive off coordinated water and allow the Cu(II) ions to occupy sites in hexagonal cavities exhibited a very broad asymmetric line (see Figs. 5h and i discussed below). Such a weak, broad line would be readily masked by the resonance lines of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$. Thus, although there may be some layers present which contain Cu(II) in layers devoid of water, especially in those samples with $F = 0.6$ and 1.0 , they could not be detected.

When each of the Cu(II) RCM samples was exposed to water vapor for 24 hr, an intense isotropic Cu(II) signal appeared, centered near $g = 2.17$. The anisotropic signal characteristic of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ was very weak for the samples with $F = 0.6$ and 1.0 and completely absent at $F = 0.0$ and 0.2 . The isotropic signal arises because of rapid tumbling or interchange of dynamic Jahn-Teller states for the fully hydrated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ions (Clementz *et al.*, 1973). Most of the fully hydrated Cu(II) ions at $F = 0.0$ and 0.20 undoubtedly exist in interlayers containing several molecular layers of water, but at $F = 0.6$ and 1.0 a large fraction of the ions probably occupy external exchange sites. It was desirable, therefore, to elucidate further the nature of the external exchange sites on the reduced charge mineral.

The end-member, $F = 1.0$, was selected for detailed investigation. Figure 4(a) shows the e.s.r. spectrum of the air-dry, Li(I)-Na(I) RCM before Cu(II) saturation. The sharp resonance near $g = 2.0$ is due to some paramagnetic constituent of the native clay that has not yet been fully characterized (Angel and Hall, 1972; Friedlander *et al.*, 1963; Wauchope and Haque, 1971). Figure 4(b) shows the powder spectrum of air-dry Cu(II)-saturated RCM at $F = 1.0$. It is obviously unsatisfactory from the standpoint of characterizing the g_{\parallel} component due to the combined effects of sloping baseline

Table 1. Cation exchange capacity and e.s.r. data* for hydrated Cu(II) ion on the surfaces of reduced charge montmorillonites

F	[Cu(II)] m-equiv. 100 g^{-1}	g_{\perp} ± 0.002	$\Delta H_{\perp}^{\dagger}$ (G)	g_{\parallel} (± 0.008)	$(10^4)A/C$ (cm^{-1})
0	88	2.081	128	2.308	155
0.2	73	2.085	135	2.293	154
0.6	53	2.091	150	2.298	152
1.0	27	2.083	130	2.306	156

* All e.s.r. parameters taken from air-dry, oriented samples at room temperature.

\dagger Linewidth of the perpendicular component.

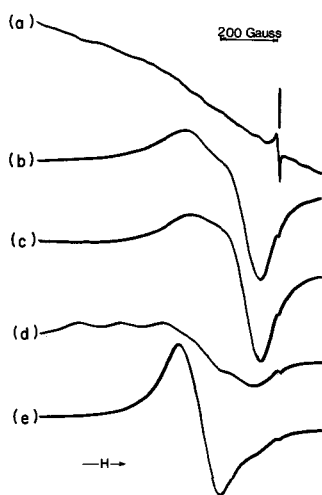


Fig. 4. E.S.R. spectra of RCM at $F = 1.0$. (a) baseline of air-dry, unexchanged Li(I)-Na(I) powder; (b) air-dry Cu(II)-saturated powder; (c and d) an air-dry, Cu(II)-saturated pressed disk with H parallel and perpendicular to the silicate layers, respectively; (e) Cu(II)-saturated powder exposed to a free-water surface for 24 hr. Field setting is identical for all samples.

and anisotropic broadening. The broad hump in the middle of the spectrum can be attributed to a small amount of isotropic Cu(II) in the system. Figures 4(c and d) illustrate the effect of orienting a pressed disk of the mineral perpendicular and parallel to the magnetic field direction. Even though complete orientation of the clay platelets is not possible in the pressed disk, results comparable with those of Fig. 3 are obtained. The isotropic signal obtained upon exposure to water vapor is illustrated in Fig. 4(e).

Figures 5(a and b) are the spectra of a pressed disk of the $F = 1.0$ Li(I)-Na(I) RCM which was washed with $\text{CuCl}_2/\text{H}_2\text{O}$ solutions to replace predominately the external sites with Cu(II) and then air-dried. The spectra are identical to those observed for $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ in which ions are present both internally and externally (Fig. 4). An isotropic signal appears upon exposure of the sample to water (Fig. 5c). These observations reveal the remarkable fact that under air-dried conditions the hydrated Cu(II) ion possesses axial symmetry and the symmetry axis is perpendicular to the surface in a tetragonal ligand field. If Cu(II) ions on crystal edges assume the same stereochemistry as those on layer surfaces then one would expect the symmetry axis to be perpendicular to the crystal edges. Thus, either the edge sites are so few in number that they cannot be detected by this e.s.r. technique or they are oriented with the symmetry axis parallel to the edges. The latter seems extremely unlikely, and we suggest that edge

sites are negligible or non-detectable. The effect of exposure of the sample to water vapor causes the ion to further hydrate, move away from the surface, and tumble rapidly. This combined behavior is very similar to that observed in zeolites (Turkevich *et al.*, 1972) with the exception that extreme dehydration conditions are required to observe an anisotropic signal for the ion on the zeolite surface.

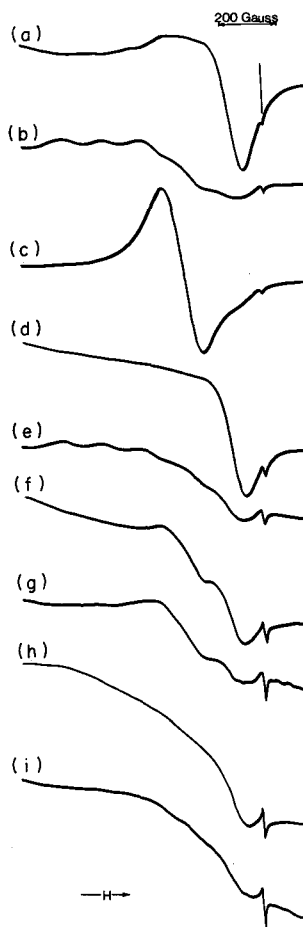


Fig. 5. E.S.R. spectra of selectively Cu(II)-saturated RCM ($F = 1.0$) pressed disks: (a and b) predominantly external Cu(II)-saturation under air-dry conditions with H parallel and perpendicular to the silicate layers, respectively; (c) the same sample after exposure to a free-water surface (essentially orientation independent); (d and e) internally Cu(II)-saturated under air-dry conditions with H parallel and perpendicular to the silicate layers, respectively; (f and g) the previous sample after exposure to a free-water surface with H parallel and perpendicular to the silicate layers, respectively; (h and i) the previous sample after heating to 200°C for 1 hr, sealed, and allowed to return to room temperature, with H parallel and perpendicular to the silicate layers, respectively.

Preferential internal Cu(II) exchange was accomplished by replacing external Cu(II) sites of totally Cu(II)-saturated $F = 1.0$ RCM with tetrabutylammonium ion. Under air-dried conditions the e.s.r. signal is orientation dependent and indicative of the tetraquo species (Figs. 5d and e). One notable difference relative to the externally saturated sample is the broadening of the g_{\perp} component. Although the g factors do not differ significantly from the external $\text{Cu}(\text{H}_2\text{O})_4^{2+}$, the ion is obviously under some axial compression and in a more restricted environment where dipolar interactions with structural Fe(III) can be more pronounced. This could account for the line broadening effects. When this sample is exposed to water (Figs. 5f and g) there is some indication of isotropic Cu(II), probably present in layers that can expand. The loss of the A_{\parallel} components of g_{\parallel} for the tetraquo ion can be attributed to the superposition of the isotropic spectrum which is orientation independent. When the sample is heated to eliminate water and permit the internal Cu(II) ion to occupy sites in hexagonal prisms in collapsed interlayers, the orientation independent, asymmetric, broad line shown in Figs. 5(h and i) is observed. The marked line broadening is attributed to enhanced dipolar interactions between Cu(II) and iron in the silicate structure. As indicated earlier, some interlayers may contain dehydrated Cu(II) in the air-dried form of the mineral, but their concentration is too low to discern by e.s.r. in the presence of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$.

In order to verify that selective Cu(II) saturation on internal and external sites was achieved for the $F = 1.0$ RCM, the Cu(II) CEC was determined for both samples. The results are compared in Table 2 with the CEC of the corresponding totally Cu(II)-saturated RCM. The sum of the CEC for the preferentially external and internal exchange forms is only 7 per cent larger than the total CEC. A positive deviation is expected based on a consideration of the reactions used to prepare the samples. The presence of any interlayers expansible by water in the initial Li(I)-RCM at $F = 1.0$ would lead to an overestimate of the external Cu(II) CEC. On the

other hand, expansible interlayers in the corresponding Cu(II) RCM would cause the internal CEC to be underestimated. The impetus for internal replacement of Li(I) by Cu(II), however, should be greater than that for internal replacement of Cu(II) by tetrabutylammonium ion. Thus, the positive error in the external CEC should exceed the negative error in the internal CEC. This argument is substantiated by the CEC data shown in Table 2 for predominantly internal and external Cu(II) exchange forms of RCM with $F = 0.6$ where there is a greater degree of interstratification and a larger number of water-expansive interlayers. The percent deviation for the sum of apparent internal and external CEC is more than twice that obtained at $F = 1.0$.

If we attribute the deviation for the sum of internal and external Cu(II) CEC at $F = 1.0$ to an overestimate of the number of external sites, then the external CEC is 20 m-equiv/100 g. An identical CEC was obtained by Brindley and Ertem (1972) for NH_4^+ exchange of Li(I) RCM at $F = 1.0$, and this value probably is also an accurate estimate of the external CEC. It has been estimated previously that approximately 20 per cent of the total CEC of montmorillonite is due to the presence of external sites (Grim, 1968). Therefore, it is somewhat surprising that the external CEC of RCM at $F = 1.0$ is so large. It would appear that the Li(I) migration into octahedral sites in internal silicate layers is preferred over migration into octahedral sites in the silicate layers at the external surface. However, it is conceivable that there is no preferential Li(I) migration, but that the Li(I) ions which migrate into the octahedral sites of the surface layers upon heat treatment can migrate out of these sites onto the external surface when the external surface of the mineral is solvated. Further studies are needed, however, to test this latter hypothesis.

CONCLUSIONS

Several important features of reduced charge montmorillonite have been revealed in this study. Regardless of the amount of charge reduction, complete

Table 2. Cation exchange data obtained by conductometric titration of selectively Cu(II)-saturated RCM's

Sample	Primary type of exchange site	[Cu(II)] m-equiv 100 g ⁻¹	Sum of internal and external CEC	% Deviation
$F = 1.0$	Total CEC	27	29	7
	External	22		
	Internal	7		
$F = 0.6$	Total CEC	53	65	18
	External	28		
	Internal	37		

exchange of cations on both internal and external sites can be accomplished if the proper solvent is selected. Moreover, at maximum charge reduction a combination of solvents can be used to selectively saturate internal and external sites with different ions.

When Cu(II) is the exchangeable ion, the predominant type of external site is on the planar surfaces of the crystallite; the number of edge sites are believed to be negligible. There are three types of interlayers which can contain Cu(II) ions: (1) interlayers of hydrated Cu(II) which can expand upon hydration; (2) those which contain water coordinated to Cu(II) but cannot be expanded beyond a monolayer by water; and (3) interlayers which are completely collapsed with Cu(II) within hexagonal prisms of silicate oxygens. At high surface charge values (corresponding to $F = 0.0$ and 0.2) the majority of Cu(II) ions are in interlayers of the first type. As the surface charge is reduced, the fraction of interlayers of the second and third type increases. However, at maximum charge reduction ($F = 1.0$) approximately 75 per cent of the copper ions occupy external sites.

Under air-dried conditions most of the copper ions, whether on external sites or in interlayers of the first and second type, exist as the tetraaquo-species $\text{Cu}(\text{H}_2\text{O})_4^{2+}$, and the symmetry axis of the ion is oriented perpendicular to the silicate sheets. Upon exposure to a full partial pressure of water vapor, the ions on external sites and those in layers which will expand become completely hydrated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ and tumble rapidly. The $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ species in non-expandable interlayers maintain their restricted orientation on the silicate surface.

One may regard RCM as being heterogeneous with respect to layer charge distribution. The charge heterogeneity results in differential response to Cu(II)-saturation. Those layers possessing very low charge may collapse and in the process, desolvate the ion. Layers of intermediate charge may allow one hydrated layer to exist, but opposing forces (i.e. van der Waals attraction and coulombic repulsion, as well as the energy required to desolvate the ion) prevent either further contraction or expansion by water. Those layers with somewhat greater charge density may exhibit greater swelling tendencies. But in all cases the presence of

ions in the interlamellar space can serve as a 'wedge' to reexpand the layers when a suitable solvent is available. When ions such as lithium and sodium are present on the exchange sites of these low charge montmorillonites one expects there to be a greater proportion of collapsed layers since their enthalpies of hydration are only one fourth and one fifth, respectively, of that for Cu(II).

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Résumé—Une série de montmorillonites Cu(II) à charge réduite dans des proportions variables (RCM) a été préparée par échange du minéral initial Li(I)–Na(I) avec CuCl_2 en solution éthanol à 95 pour cent. La capacité d'échange Cu(II) déterminée par l'échange de Na(I) dans des solutions éthanol–eau 1:1 (v/v), est une fonction linéaire de la fraction de Li(I) initialement présent sur les sites d'échange, F . La saturation sélective en Cu(II) des sites internes et externes est obtenue par une réduction maximale de la charge ($F = 1.0$). Les isothermes d'adsorption d'eau et les espacements basals (001) sont interprétés en termes d'une tendance croissante à la fermeture des espaces interfeuilletés avec une réduction de charge croissante. Cependant, à cause de l'énergie d'hydratation plus élevée de l'ion Cu(II), la fraction d'espaces interfeuilletés non expansibles à une valeur donnée de F est plus basse

que celle que l'on trouve dans la RCM Li(I)–Na(I) correspondante. Les spectres de résonance de spin électronique d'échantillons orientés montrent qu'en conditions air-dry (40 pour cent d'humidité relative), l'espèce Cu(II) prédominante aussi bien sur les sites internes que sur les sites externes, est l'ion plan $\text{Cu}(\text{H}_2\text{O})_4^{2+}$.

L'axe de symétrie de l'ion est orienté perpendiculairement au plan ab des feuillet. En présence d'une pression partielle de vapeur d'eau saturante, les ions Cu(II) des sites externes et ceux qui sont dans les espaces interfeuillet expansibles s'hydratent totalement en ions $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ et prennent rapidement une orientation quelconque. Les ions $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ dans les espaces non expansibles gardent leur orientation privilégiée par rapport à la surface. Des conclusions générales sont tirées à propos de la nature de la distribution de la charge dans le minéral.

Kurzreferat—Aus einem ursprünglich Li(I)–Na(I)-belegten Mineral wurde durch Austausch mit CuCl_2 in 95 prozentsatz iger Äthanollösung eine Reihe von Cu(II)-belegten Montmorilloniten verminderter Ladung (RCM) mit unterschiedlicher Ladungsabnahme hergestellt. Die Cu(II)-Austauschkapazität, bestimmt durch Na(I) in einem Äthanol–Wasser–Gemisch im Volumenverhältnis 1:1, ist eine lineare Funktion des ursprünglich an den Austauschplätzen vorliegenden Li(I). F. Selektive Cu(II)-Sättigung an inneren und äußeren Austauschplätzen wurde bei maximaler Ladungsverminderung ($F = 1,0$) erreicht. Die Wasseradsorptionsisothermen und (001)-Basisebenenabstände wurden als Ergebnis einer mit zunehmender Ladungsverminderung steigenden Neigung zur Zwischenschichtkontraktion gedeutet.

Wegen der höheren Hydratationsenergie des Cu(II)-Ions ist jedoch der Anteil der nichtaufweitbaren Zwischenschichten bei gegebenem F-Wert niedriger als der Anteil in den entsprechenden Li(I)- und Na(I)-belegten RCM.

Elektronenspinresonanzspektren orientierter Proben zeigen, daß unter lufttrockenen Bedingungen (ca. 40 prozentsatz relative Feuchte) sowohl an den inneren als auch an den äußeren Austauschplätzen das planare $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ -Ion die vorherrschende Zustandsform des Cu(II) darstellt. Die Symmetrieachse des Ions ist senkrecht zur a - b -Ebene der Silicatschichten angeordnet. Bei Vorliegen eines vollen Wasserpartialdruckes werden Cu(II)-Ionen an den äußeren Oberflächen und an den aufweitbaren Zwischenschichten zu vollständig hydratisierten $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ -Ionen und gehen schnell in einen ungeordneten Zustand über. Die $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ -Ionen in den nichtaufweitbaren Schichten behalten ihre eingeschränkte Orientierung an den Silicatoberflächen. Einige allgemeine Schlußfolgerungen bezüglich der Art der Ladungsverteilung im Mineral werden gezogen.

Резюме — Ряд Cu(II) монтмориллонитов с уменьшенным зарядом (RCM) до различных степеней готовится путем обмена маточного минерала Li(I)–Na(I) с CuCl_2 в 95% растворе этанола. Способность обмена Cu(II), определяемая обменом Na(I) в 1 : 1 (процентное соотношение объемов) этанола-воды, является линейной функцией фракции Li(I) первоначально присутствующей на позициях обмена, F. Селективное насыщение Cu(II) на внутренних и наружных позициях получается путем максимального понижения заряда ($F = 1,0$). Изотермы адсорбции воды и основные позиции (001) истолковываются повышающейся тенденцией к разрушению прослойки при возрастающем уменьшении заряда. Однако вследствие более высокой энергии гидратации иона Cu(II), фракция нерасширяющихся промежуточных слоев при определенной величине F ниже, чем присутствующая в соответствующем Li(I)–Na(I) RCM. Резонансный спектр электронного спина ориентированных образцов показывает, что в воздушно-сухих условиях (около 40% относительной влажности) объектом Cu(II), присутствующим главным образом на внутренних или наружных позициях, является плоский ион $\text{Cu}(\text{H}_2\text{O})_4^{2+}$. Ось симметрии иона находится перпендикулярно к плоскости a - b силикатных листов. В присутствии полного частичного давления воды, ионы Cu(II) на наружных позициях и те которые находятся на расширяющихся промежуточных слоях становятся полностью гидратированным ($\text{Cu}(\text{H}_2\text{O})_6^{2+}$ и быстро падают. Ионы $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ на нерасширяющихся слоях сохраняют свою строгую ориентацию на поверхности силиката. Пришли к общим заключениям о характеристике распределения заряда в минерале.