THE NATURE OF HYDRATED COPPER (II) IONS IN LAYER SILICATES

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
DAVID MICHAEL CLEMENTZ
1973

This is to certify that the

thesis entitled

THE NATURE OF HYDRATED
COPPER (II) IONS IN LAYER SILICATES

presented by

David Michael Clementz

has been accepted towards fulfillment
of the requirements for

Ph. D. degree in Soil Science

Major professor

Date July 18, 1973

O-7639

ABSTRACT

THE NATURE OF HYDRATED

COPPER (II) IONS IN LAYER SILICATES

By

David Michael Clementz

The stereochemistry of hydrated Cu (II) ions on the interlamellar surfaces of microcrystalline layer silicates has been investigated by observing the anisotropic components of the g factor in the esr spectra of oriented film samples at room temperature. When a monolayer of water occupies the interlamellar regions the ion has axial symmetry and the symmetry axis is perpendicular to the silicate layers. The Cu (II) ion most likely is coordinated to four water molecules in the xy plane and to two silicate oxygens along the z axis. Under conditions where two layers of water occupy the interlamellar regions, the ion is in an axially elongated tetragonal field of six water molecules and the symmetry axis is inclined with respect to the silicate layers at an angle near 45°. If several layers of water molecules occupy the interlamellar regions, the $Cu(H_2O)_6^{2+}$ ion tumbles rapidly and gives rise to a single, isotropic esr signal analogous to that normally observed for the ion at temperatures above 50° K.

A series of Cu (II) reduced charge montmorillonites (RCM) of varying charge reduction was then prepared by exchange of the parent

Li(I)-Na(I) mineral with $CuCl_2$ in 95% 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 adsorption 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-expandable interlayers at 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% relative humidity) the predominant Cu (II) species present, whether on internal or external sites, is the planar $Cu(H_2O)_4^{2+}$ 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 expandable interlayers become totally hydrated ($Cu(H_2O)_6^{2+}$) and tumble rapidly. The $Cu(H_2O)_4^{2+}$ ions in non-expandable layers retain their restricted orientation on the silicate surface. Some general conclusions have been drawn regarding the nature of charge distribution in the mineral.

THE NATURE OF HYDRATED COPPER (II) IONS IN LAYER SILICATES

By

David Michael Clementz

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

Department of Crop and Soil Sciences

1973

ACKNOWLEDGMENTS

The author wishes to express appreciation to his major professor Dr. Max M. Mortland for sharing his unremitting enthusiasm for research. Dr. Mortland's imagination and high standards have allowed the author to develop as a scientist while pursuing broad personal interests.

Gratitude is also expressed to Dr. Thomas J. Pinnavaia for his relentless barrage of questions during this study which encouraged the author to expand his capabilities and philosophy toward research. In addition, appreciation is expressed to the MSU Chemistry Department for the use of their equipment and to Dr. Roger V. Lloyd for obtaining the Q-band spectra.

Personal thanks are extended to Dr. Bernard D. Knezek who was primarily responsible for my coming to MSU and to his family for their hospitality during our stay.

Appreciation is also expressed to Dr. T. A. Vogel and Dr. B. G. Ellis for serving on the committee.

Words cannot express the special thanks due to the author's wife Carol, for her patience, understanding, and steadfast devotion during the course of his graduate studies and for the typing of this manuscript.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PART II PAGE

INTRODUCTION

The nature of hydrated copper (II) ions in layer silicates is of interest from several viewpoints. First, copper (II) is an essential element required for plant nutrition. Yet it can become a pollutant at high concentrations. This paradox automatically draws our attention since Cu (II) can adhere to the exchange sites on layer silicates present in soils and sediments. Secondly, Cu (II) has recently been shown to have unique ability to coordinate aromatic molecules when present on layer silicate surfaces. Coupled to these interests are the electronic configuration and nuclear properties of Cu (II) itself which allow it to be studied via electron spin resonance (esr) spectroscopy.

Esr has been recognized as a powerful tool in examination of Cu (II) ions in various environments. However, very few esr studies of Cu (II) ions in layer silicates have been made. To the author's knowledge, no studies to date have shown in what hydrated form Cu (II) exists on exchange sites of layer silicates or what accounts for its unique coordinating abilities on these surfaces. Clearly, any attempt to make such observations must come from studying the

Cu (II) ion *in situ* and esr is particularly suited for this task.

Once the nature of the ion is understood in known submicroscopic environments, it can be introduced into unknown systems and therein reflect its environment. Therefore, this study was made in two parts. The first involved investigating the stereochemistry of hydrated copper (II) ions in a representative variety of layer silicates which are well characterized by the latest chemical and physical methods. Once that data was obtained, the Cu (II) ions were introduced onto the exchange sites of artificially altered minerals and used to describe some of their properties.

PART I

Stereochemistry of Hydrated Copper (II) Ions on the Interlamellar Surfaces of Layer Silicates. An Electron Spin Resonance Study

Introduction

Recent investigations have shown that Cu (II) ions can form complexes with various aromatic molecules when present at the interlamellar cation exchange sites of certain layer silicate minerals, known as montmorillonites, or better, smectites.[1-5] The silicate layers undoubtedly play an important role in stabilizing the complexes since Cu (II) in other environments, including homogeneous solution as well as the solid state, is not known to form arene complexes. In view of this observation, information concerning the nature of Cu (II) ions on layer silicate surfaces is of interest.

The objective of the present work was to investigate the stereochemistry of exchangeable hydrated Cu (II) ions in the interlamellar regions of various layer silicates by means of esr spectroscopy. Although the minerals are microcrystalline, they are potentially well suited for such studies because highly ordered films can be prepared in which the crystallites are oriented with their planes of hydrated metal ions parallel to each other. Thus it should be possible to deduce the orientations of the anisotropic components of g with respect to the anionic silicate surface. Although esr

spectroscopy has been used to study hydrated Cu (II) and other paramagnetic ions in amorphous resins,[6] isotropic zeolites,[7] and layer silicates,[8] the special utility of the technique when applied to oriented samples of the latter types of compounds has been only recently recognized.[8c]

All of the layer silicates investigated in the present study are related in that the silicate layers consist of two silica sheets that enclose an octahedral layer which is occupied by non-exchangeable cations such as Al(III), Fe(III), Mg(II) and Li(I). The negative charge on the infinite two-dimensional silicate framework originates from positive charge deficiencies in the octahedral layer or by the replacement of Si(IV) by a trivalent ion (eg., Al(III)) in the tetrahedral silica sheets. Minerals of both types were investigated in order to assess the effect of the site of positive charge deficiency in the silicate framework on the stereochemistry of the hydrated Cu (II) ions in the interlamellar regions.

Experimental Methods

The following naturally occurring layer silicates of known unit cell composition were used: Hectorite (Hector, California); Montmorillonite (from Upton, Wyoming', Chambers, Arizona', and Otay, California); Saponite (Scotland), and Vermiculite (from Llano, Texas', and Libby, Montana). The Cu (II) exchange forms were prepared by slurrying for several hours ca. 2.0 g of the $< 2\mu$ fraction of the mineral in 500 ml of an aqueous or methanol solution of 1.0N $CuCl_2$, centrifuging, and discarding the supernatant liquid. The procedure was repeated three times, and then the excess chloride was removed

by washing with water or methanol until a negative chloride ion test with $AgNO_3$ was obtained. Each sample was given a final wash with methanol, dried in air, and then allowed to stand several days at 100% relative humidity to displace any adsorbed methanol with water. The sodium exchange forms were prepared in an analagous fashion, except that the exchange reactions were carried out in aqueous solution, and the products were isolated from aqueous suspension by freeze-drying.

The esr spectra of randomly oriented powder samples of the sodium exchange forms were recorded to identify the resonances due to non-exchangeable paramagnetic ions in the silicate layers. Only the vermiculite from Libby, Montana, exhibited a very broad (ΔH = 320 Gauss) resonance with a g value near 2.0. This resonance is believed to be due to iron (III) ions which occupy octahedral positions in the silicate layers as similar spectra have been observed previously [9] for hydromicas in which Fe(III) ions occupy octahedral environments. Although the sodium exchange form of each of the other silicates gave resonance signals near g = 4.0, which may arise from Fe(III) in tetrahedral sites,[10] none showed resonances near g = 2.0 which were sufficiently intense to obscure Cu (II) signals in X-band spectra. In the case of the Libby vermiculite, the Cu (II) signals could be resolved from the iron signal in the Q-band spectrum at 77° K. Some dipolar interactions probably occur between iron and copper, because the width of the copper resonances increased with increasing iron concentration in the silicate layer.

In general, highly ordered self-supporting films of the Cu (II) exchange forms of the layer silicates were prepared by evaporating at room temperature an aqueous suspension of the mineral on a flat

polyethylene or teflon surface and then peeling the films away. Since the crystallites are oriented with their silicate layers parallel to the film surface, narrow strips of film (ca. 3 x 10 mm) placed vertically in a 4 mm quartz glass esr tube or on a teflon holder could be positioned in the cavity of an esr spectrometer with the silicate layers at a known angle to the external magnetic field. Films of the montmorillonite sample from Otay, California, exhibited poor mechanical strength, suggesting that only partial orientation of the crystallites occurs upon evaporation of the suspension. In this case, however, an esr spectrum for a partially oriented sample was obtained by evaporating the suspension on a thin teflon strip and placing the entire strip in an esr tube.

Esr X-band spectra were obtained with a Varian E-4 spectrometer; the Q-band spectrum for Cu (II) was recorded on a Varian Model V4503 Q-band spectrometer. A Phillips X-ray diffractometer with copper radiation and a nickel filter was used to determine the (001) spacings of the copper (II) exchange forms of the layer silicates.

Results and Discussion

Hectorite is an example of a layer silicate in which the negative charge on the silicate layers originates exclusively from a positive charge deficiency in the octahedral positions. When allowed to equilibrate in air under ambient conditions, the Cu (II) exchange form exhibits a 001 spacing of 12.4Å and a water to copper ratio of about 8:1. Since the silicate lattice c dimension is 9.6Å, the thickness of the interlamellar region (2.8Å) indicates that the Cu (II) ions are hydrated by a monolayer of water molecules.

Esr spectra of the Cu (II) ions under these conditions are illustrated in Figure 1. Spectra A and B for randomly oriented powder samples at room temperature and at 77° K, respectively, consist of clearly defined $g_{\perp}$ and $g_{\parallel}$ components as expected for Cu (II) with axial symmetry and $(g_{\parallel} - g_{\perp})\beta H > hA$. Although hyperfine splitting due to ^{63}Cu and ^{65}Cu (I=3/2) is well resolved for the parallel component, none was observed for the perpendicular component. When the spectrum of an oriented film sample is recorded with the silicate layers parallel to the magnetic field direction (cf., spectrum C) only $g_{\perp}$ is observed. On the other hand, when the film is oriented with the silicate layers perpendicular to H, only the $A_{\parallel}$ components of $g_{\parallel}$ are visible. Thus the symmetry axis of the hydrated ion is positioned perpendicular to the silicate layers.

The esr results, together with the fact that a monolayer of water occupies the interlamellar region, are consistent only with an environment in which copper (II) is coordinated to water molecules in the xy plane and to surface oxygens of the silicate lattice along the z axis. Most likely, four water molecules are bound to copper as shown schematically in Figure 2A. The remaining water molecules must occupy outer spheres of coordination. If most of this latter water is removed by heating the silicate under vacuum at 110°, the esr spectral features of an oriented film sample remain unchanged. Thus the amount of outer sphere water, which has been recently described by Farmer and Russell[11] as forming a dielectric link between the exchangeable cation and the silicate surface, does not alter the basic stereochemistry of the ion.

The esr spectral parameters for air-dried Cu (II) Hectorite are presented in Table 1 (Part A) along with those for related Cu (II)

Figure 1. Esr spectra (first derivative curves) for Cu (II) hestorite. A and B) randomly oriented powder samples at 300 and 77°K, respectively, C) oriented film sample at 300° K with the a,b-planes of the silicate layers positioned parallel to H. D) a,b-planes positioned perpendicular to H.

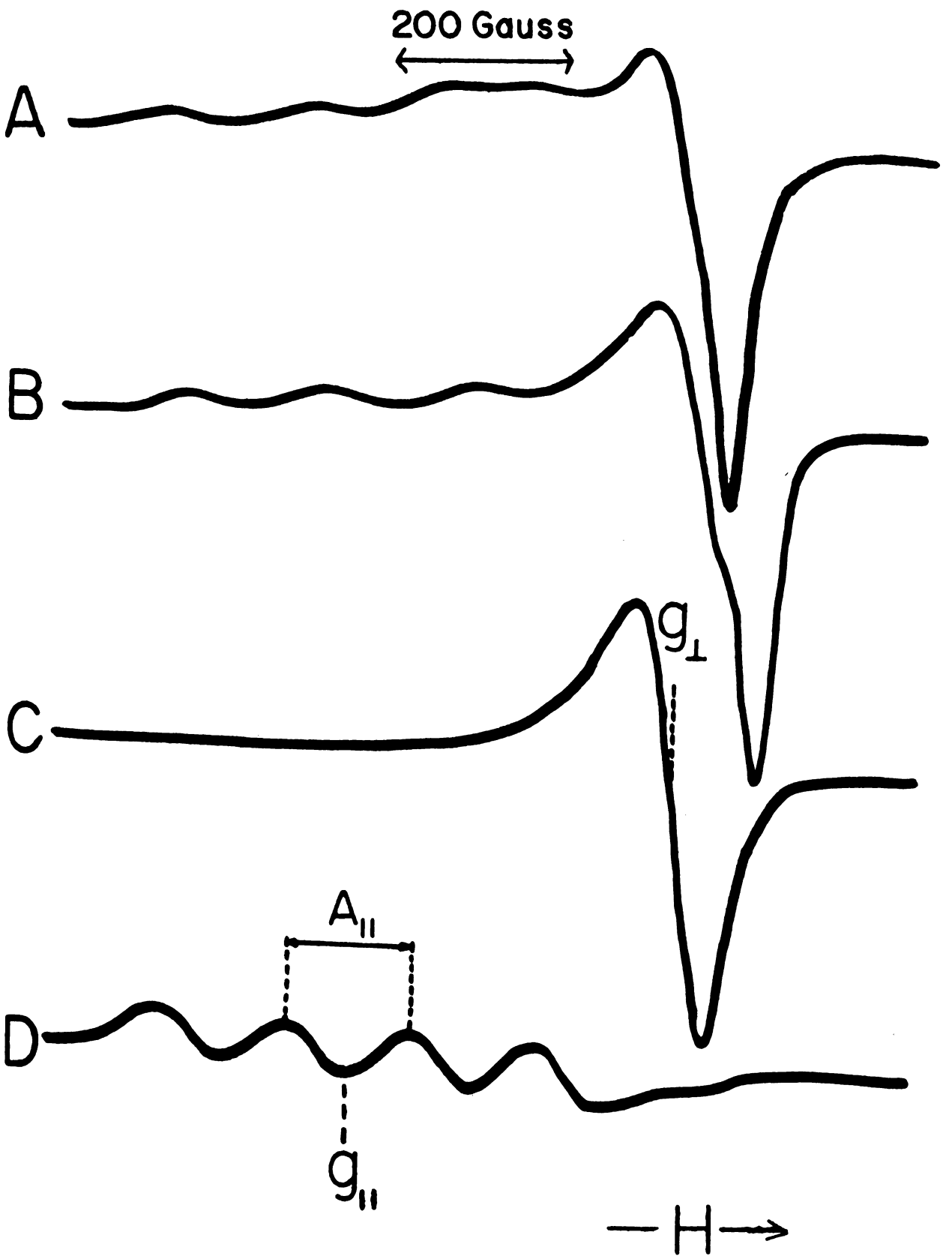

Figure 1

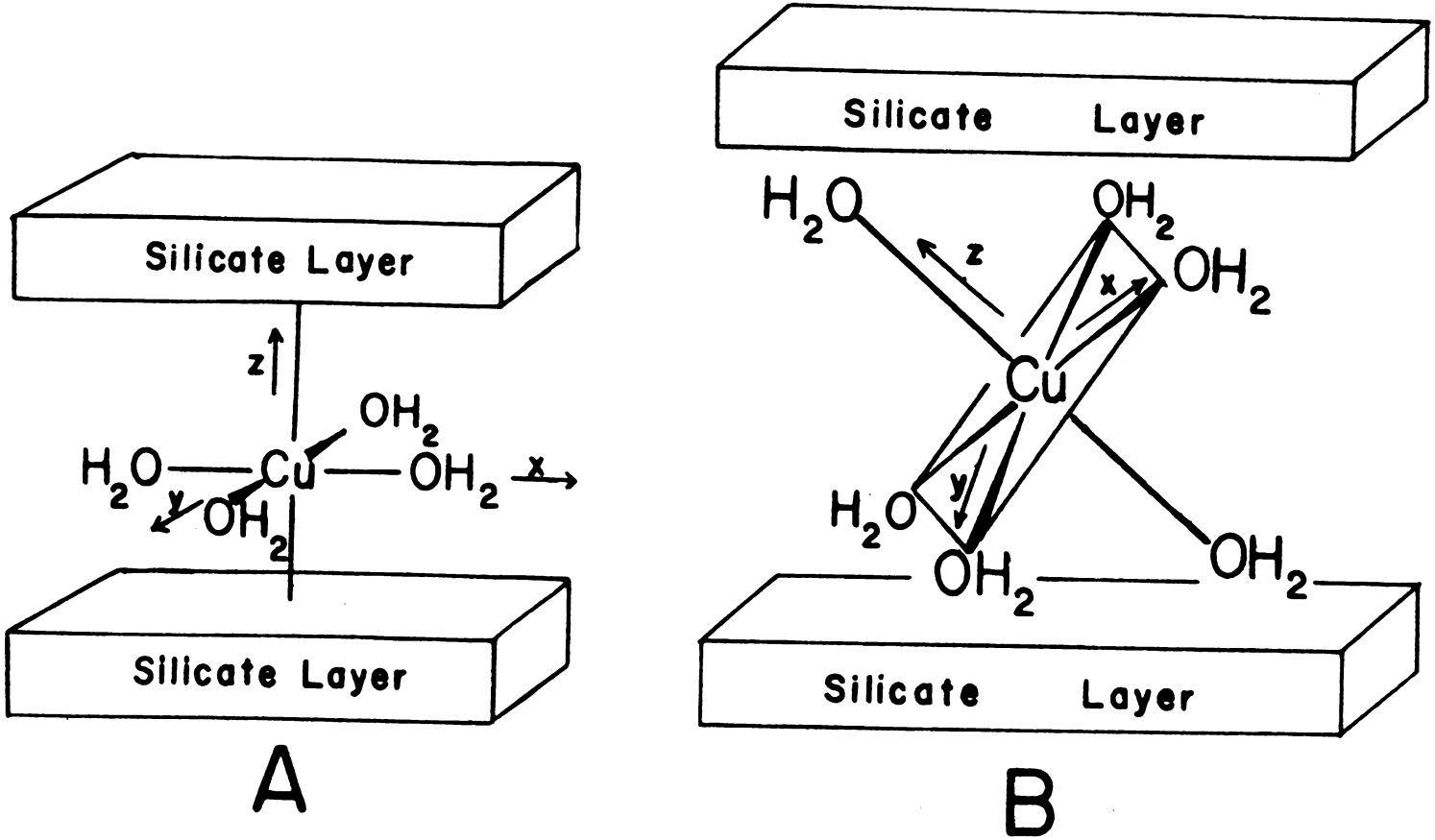

Figure 2. Schematic representation of the stereochemistry of hydrated Cu (II) under conditions where (A) one layer and (B) two layers of water occupy the interlamellar regions.

Table 1. Esr Data for Hydrated Cu(II) Ions on the Interlamellar Surfaces of Various Layer Silicates.

Layer Silicate	Unit Cell Formula [a]	Temp, °K	$g_{\perp}$	$\Delta H_{\perp}$, [b] Gauss	$g_{\parallel}$	$10^4 A_{\parallel}$, cm^{-1}	g_{av} [c]
A. Interlamellar Regions Occupied by a Monolayer of Water [d]							
Hectorite	$Cu_{0.21}[Mg_{5.42}\ Li_{0.68}\ Al_{0.02}](Si_{8.00})O_{20}(F,OH)_4$	300	2.08	100	2.34	165	2.17
		77	2.08	100	2.33	175	2.16
Montmorillonite (Upton, Wyoming)	$Cu_{0.32}[Al_{3.06}\ Fe_{0.32}\ Mg_{0.66}](Al_{0.10}\ Si_{7.90})O_{20}(OH)_4$	77	2.09	158	2.34	175	2.17
Montmorillonite (Chambers, Arizona)	$Cu_{0.48}[Al_{2.84}\ Fe_{0.35}\ Mg_{0.85}](Al_{0.22}\ Si_{7.78})O_{20}(OH)_4$	77	2.09	140	2.33	175	2.16
Montmorillonite (Otay, California)	$Cu_{0.63}[Al_{2.69}\ Fe_{0.11}\ Mg_{1.20}](Al_{0.05}\ Si_{7.95})O_{20}(OH)_4$	77	2.09	120	2.33	190	2.17
Saponite	$Cu_{0.51}[Mg_{5.82}Mn_{0.01}Al_{0.04}Fe_{0.08}](Al_{1.00}Si_{7.00})O_{20}(OH)_4$	300	2.08	90	2.35	145	2.17
		77	2.08	125	2.35	180	2.16
Vermiculite (Llano, Texas)	$Cu_{1.00}[Al_{0.30}\ Fe_{0.02}\ Mg_{5.66}](Al_{2.28}\ Si_{5.72})O_{20}(OH)_4$	300	2.10	~80	~2.3	[e]	
B. Interlamellar Regions Occupied by Two Layers of Water [f]							
Vermiculite (Llano, Texas)	(see above)	300	2.10	45	2.40	115	2.20
Vermiculite (Libby, Texas)	$Cu_{0.95}[Al_{0.14}\ Fe_{1.06}\ Mg_{4.38}](Al_{2.16}\ Si_{5.84})O_{20}(OH)_4$	77	2.16	320	2.38	145	2.23

[a] Water of hydration is omitted from the unit cell formula; cations enclosed in brackets fill octahedral positions in the silicate layer, whereas those enclosed in parenthesis fill tetrahedral positions. Sources of the unit cell formulae are as follows: Hectorite, American Petroleum Institute, Research Project 49; Upton Montmorillonite, G. J. Ross and M. M. Mortland, Soil Sci. Soc. Amer. Proc., 30, 337(1966); Otay and Chambers Montmorillonites, L. G. Schultz, Clays Clay Min., 17, 115(1969); Saponite, R. C. Mackenzie, Min. Mag., 31, 672(1957); Llano and Libby Vermiculites, M. D. Foster, Clays Clay Min., 10, 70(1961).
[b] Maximum line width of the perpendicular component. [c] Calculated average value of g. [d] Except for Cu(II) vermiculite, which was dried over P_2O_5, monolayers of water were obtained by allowing the samples to dry in air at room temperature. [e] $A_{\parallel}$ not resolved, due to presence of paramagnetic impurity. [f] Two layers of water were obtained by allowing the samples to dry in air.

layer silicates under conditions where a monolayer of water occupies the interlamellar regions. In each case an anisotropic spectrum with $g_{\perp}$ and $g_{\parallel}$ components was observed at room temperature but the hyperfine splitting of the parallel component was better resolved at 77° K.

Among the three montmorillonite samples shown in the table, 77 to 95% of the net negative charge on the silicate layers originates from cationic charge deficiencies in the octahedral sheet of the silicate framework, but the number of Cu (II) ions per unit cell and the nature of the ions occupying octahedral position differ from those in hectorite. Since the surface area of one face of the unit cell in all of these silicates is approximately 50 Å^2, the average distance between Cu (II) ions is ca. 16 Å in hectorite and ca. 9.0-12.5 Å in the montmorillonites. In saponite, and the two vermiculites, where all of the negative charge on the silicate layers is due to positive charge deficiencies in the tetrahedral sheets, the average distance between Cu (II) ions are estimated to be 10 and 7 Å, respectively.

Despite these differences in Cu (II) - Cu (II) distances, position of positive charge deficiency in the silicate layers, and the nature of the metal ions in the octahedral and tetrahedral sheets of the silicate framework, oriented film samples of each layer silicate showed the same esr spectral changes as those described for Cu (II) hectorite when the film is positioned parallel and perpendicular to the applied magnetic field. Moreover, in each case the magnitude of $g_{\parallel}$ is greater than $g_{\perp}$ (cf., Table 1). This result is consistent with Cu (II) ion in an axially elongated tetragonal crystal field and the unpaired electron occupying a $d_{x^2-y^2}$ orbital.[12] Axial

elongation is also indicated by the magnitudes of the interlamellar thicknesses. In the case of Cu (II) hectorite, where the interlamellar thickness is 2.8 Å, if the radius of a silicate oxygen atom is taken to be 1.4 Å , [13] then the copper (II) silicate oxygen bond length is ca. 2.8 Å . The expected distance of the Cu-OH_2 bonds is ca. 2.0 Å.[13] An example of the esr spectra obtained for an oriented film of Cu (II) montmorillonite is provided in Figure 3A.

We turn now to the deduction of the stereochemistry of hydrated Cu (II) ions when two layers of water molecules occupy the interlamellar region. Earlier X-ray diffraction studies of layer silicates [14] indicate that when two layers of water are present, divalent metal ions should be octahedrally coordinated to six water molecules. However, in the case of Cu (II) the octahedron should be distorted, as required by the Jahn - Teller theorem.

Vermiculite is especially well suited for obtaining two layers of water molecules in the interlamellar regions as the high surface charge density permits a maximum of only two layers even when the silicate is fully hydrated. Samples of the other layer silicates with all interlamellar regions uniformly occupied by two layers of water molecules are more difficult to achieve as they can be swelled beyond two layers of water molecules and thus tend to give interstratified systems.

The presence of two layers of water molecules in the interlamellar regions of air-dried oriented film of Llano Cu (II) vermiculite was verified by observing X-ray reflections of several rational orders that corresponded to a 001 spacing of 14.2Å. The esr spectrum of the film at room temperature consisted of $g_{\parallel}$ and $g_{\perp}$ components when the silicate layers were positioned both parallel and perpendicular to the

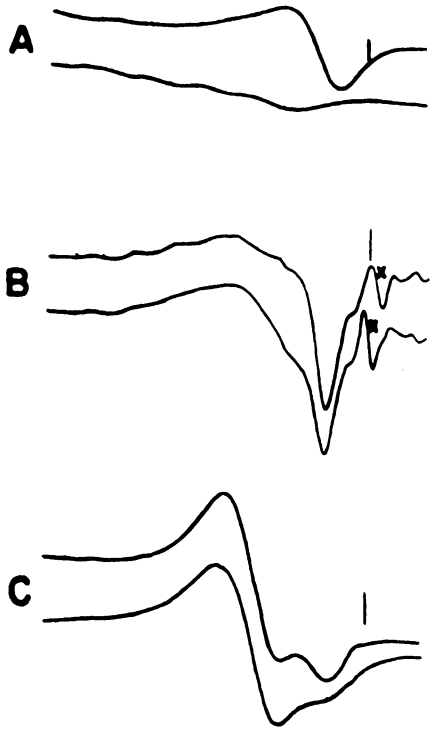

Figure 3. Esr spectra (1000 Gauss scans at 300°K) of Cu (II) in oriented film samples of layer silicates. In each case the top spectrum is for the a,b-planes positioned parallel to H, and the bottom spectrum is for the a,b-planes positioned perpendicular to H. A) Cu (II) montmorillonite (Upton) when a monolayer of water occupies the interlamellar regions. B) Cu (II) vermiculite (Llano) with two layers of water in the interlamellar region; "x" denotes an unidentified resonance line which was also observed in the Na(I) exchange form. C) Interstratified Cu (II) montmorillonite (Chambers) with varying layers of water in the interlamellar regions. H increases from left to right, and the vertical line indicates the resonance position of a standard pitch sample with g = 2.0028.

external magnetic field as shown in Figure 3B. The lack of any appreciable change in the relative intensities of $g_{\parallel}$ and $g_{\perp}$ upon altering the position of film in the magnetic field indicates that the symmetry axis of the tetragonal ion is inclined with respect to the silicate surface at an angle near 45^{o}. Also, the Cu-OH_2 bonds along the symmetry axis are longer than those in the xy plane, as $g_{\parallel} > g_{\perp}$. A schematic representation of the stereochemistry of the ion is shown in Figure 2B.

Anisotropy in the g factor of $Cu(H_2O)_6^{2+}$ is rarely observed at room temperature. One previous example was reported by Fujiwara and his co-workers in a study of cupric sulfate solutions confined in the molecular space of polyvinylalcohol gels.[15] But isotropic thermal motions are normally sufficiently rapid above $50^{o}K$ to give a single esr line.[16] One suggested motion involves the rapid exchange of the ion between three equivalent Jahn - Teller distorted states which correspond to axial elongation along the three possible sets of H_2O-Cu-H_2O axes.[17] However in the absence of rapid tumbling this motion will not lead to averaging of $g_{\parallel}$ and $g_{\perp}$ when the ion is sorbed on a surface in the manner illustrated in Figure 2B.

Esr spectral parameters for two Cu (II) vermiculites with two layers of water in the interlamellar regions are presented in Table 1 (part B). The g values are somewhat larger than those found for the planar aquo complex, and the calculated average values of g are in good agreement with the observed values of g_{av} for Cu (II) in aqueous solution[18] and for $Cu(H_2O)_6^{2+}$ at the exchange sites of resins.[6] The exceptionally large line width observed for the Libby Cu (II) vermiculite is undoubtedly due to magnetic interactions between Cu (II)

and Fe (III) which is present in large amounts in the silicate framework (cf., experimental sections).

Attempts to observe the stereochemistry of Cu (II) ion hydrated by more than two water layers were complicated by interstratification of the silicate as indicated earlier. An example of the esr spectra obtained for an interstratified system is given in Figure 3C. The high field line in the figure is due to the $g_{\perp}$ component of Cu (II) ions hydrated by a monolayer, whereas the lower field line, which is orientation independent, is due to Cu (II) hydrated by two or more layers of water.

It was possible, however, to investigate the nature of the hydrated copper (II) ions when the interlamellar regions of Cu (II) hectorite were fully expanded by soaking the silicate in water for 48 hrs. Under these conditions the 001 X-ray reflection corresponded to an interlamellar thickness of about 10Å and the esr spectrum of an oriented film sample consisted of a single isotropic line with $g = 2.192$, independent of its position with respect to H. Thus when several layers of water are present the Cu (II) ion tumbles rapidly, averaging the $g_{\parallel}$ and $g_{\perp}$ components.

PART II

Properties of Reduced Charge Montmorillonites: Hydrated Cu (II) Ions as a Spectroscopic Probe.

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% of the initial C.E.C., 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.[19] These latter solvents should provide a means of replacing the exchangeable Li^+ and Na^+ ions with any desired cation.

It has been recently demonstrated that Cu (II) ions can serve as a useful probe in detecting environmental influences of silicate surfaces on exchangeable ions by electron spin resonance (esr) spectroscopy.[20] 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 adsorption 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 Methods

Preparation of RCM :

A series of RCM samples was prepared by the method of Brindley and Ertem.[19b] Suspensions of $< 2\mu$ 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 of lithium ions occupying the exchange sites prior to heat treatment, F. The F values for the four 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 (approximately 600 ml, 0.0047 gm/ml) were stirred for 24 hours to allow maximum randomization of ions and then dried into large thin films (approximately 6" by 12") on polyethylene sheets. These clay films were peeled from the polyethylene and heated for 24 hours 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% ethanol and dispersed in a Waring blender. The ethanol suspensions were concentrated, and the clay was collected by vacuum filtration. One portion of each air-dried, Li(I)-Na(I) RCM sample was saved for the water adsorption 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 hour periods in 1 N $CuCl_2$/95% ethanol solution and repeating the procedure two more times. Excess $CuCl_2$ was removed by washing with 95% 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% relative humidity for 24 hours. All of the Cu (II) ions can be exchanged off with 3 washes of $CaCl_2$ in ethanol, as verified by the loss of a Cu (II) esr 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-gram 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 minutes to complete. Excess $[Bu_4N]^+ Cl^-$ was removed by washing with water.

C. Cu (II) Saturation of External Sites. One-gram samples of untreated Li(I)-Na(I) RCM with F values of 0.6 and 1.0 were heated to 110°C for one hour 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% relative humidity. This procedure should have

rendered all of the external exchange sites Cu (II)-saturated, while the internal sites remained largely unexchanged.

Infrared Studies:

Thin films of the RCM samples were dried onto Irtran 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 700-900 cm^{-1} region as discussed by Calvet and Prost.[19a]

Charge Reduction Measurements :

Charge reduction in RCM was verified by determing the amount of exchangeable Cu (II) present in the totally-saturated Cu (II) exchange forms. A modification of the Mortland and Mellor technique[21] was used which consisted of suspending the clays in a 50:50 (v/v) mixture of 95% ethanol and water, and titrating conductrometrically with standard NaOH. The titration curves were linear with only one end-point.

Water Adsorption:

The Cu (II)-saturated samples and the unexchanged RCM's were equilibrated at 20°C for one week under seven different partial pressures of water vapor provided by various saturated salt and sulfuric acid solutions and the resulting 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 were employed.

Electron Spin Resonance :

Some degree of orientation of crystallites was necessary to give detailed spectral information. Where possible, the oriented film technique employed earlier [21] was used. Samples which did not make good oriented films (e.g., F = 1.0) were pressed into disks [8c] under 10,000 psi for three minutes 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 Figure 1). At F = 1.0, a residual CEC of 27 meq per 100 gm is retained which corresponds to about twice the negative charge arising from tetrahedral substitution of Al(III) for Si(IV) in the mineral (unit cell formula, $M(I)_{0.64}\ [Al_{3.06}Fe_{0.32}Mg_{0.66}]\ \ (Al_{0.10}Si_{7.9})O_{20}(OH)_4$).

Included in Figure 1 for comparison purposes are the data of Brindley and Ertem [19b] for exchange of Li(I)-Na(I) RCM in ammonium acetate solution. The nonlinear 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.[19c,22] The protons could migrate to octahedral sites, satisfy

Figure 1. Solid line, plot of milliequivalents of exchangeable ions on Cu (II)-saturated RCM, as determined by Na(I) exchange in 1:1 (v/v) H_2O-ethanol, versus $\underline{F}$, 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[19b].

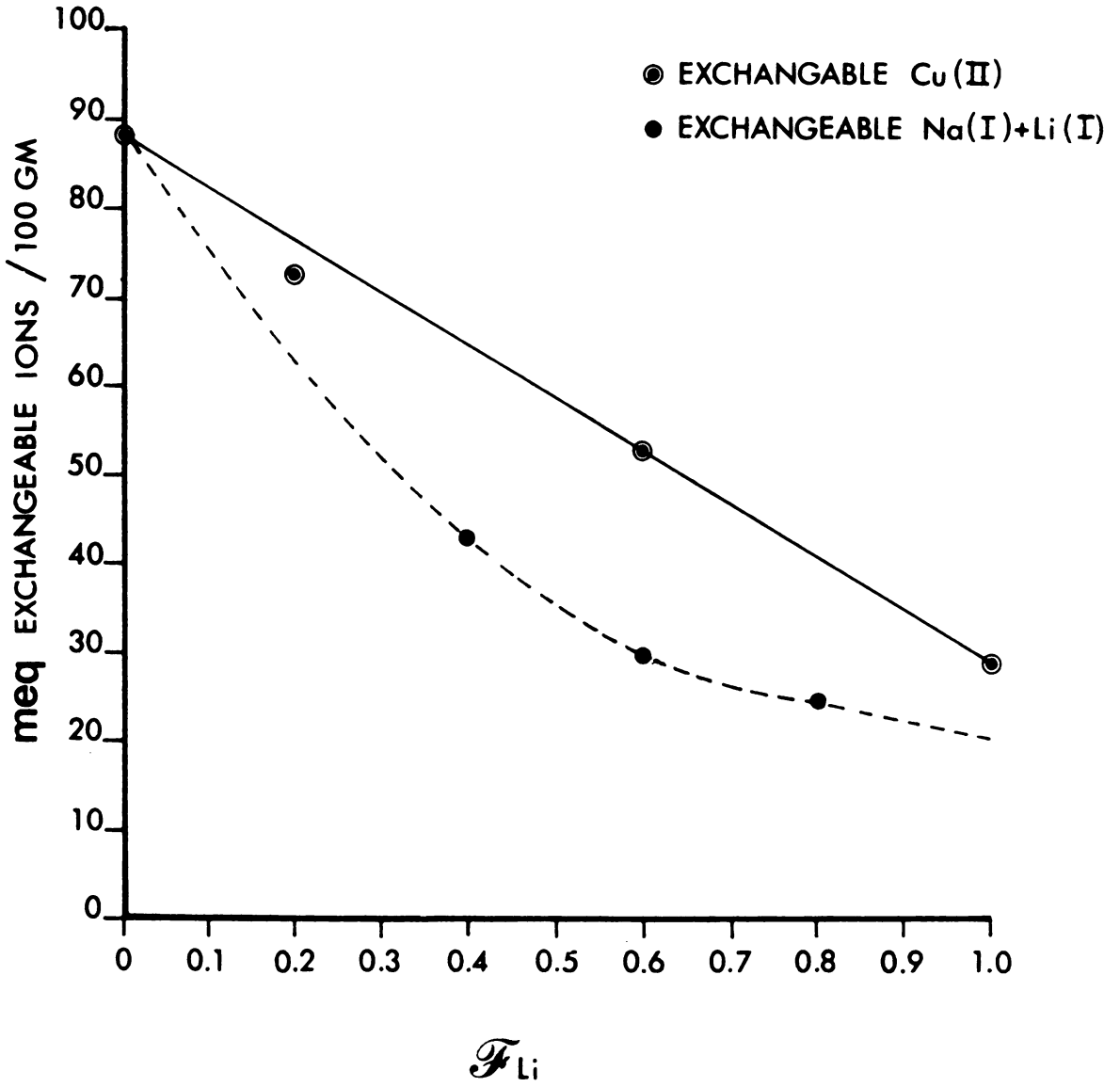
EXCHANGABLE Cu(II)
EXCHANGEABLE Na(I)+Li(I)
meq EXCHANGEABLE IONS / 100 GM
100
90
80
70
60
50
40
30
20
10
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
$\mathcal{F}_{Li}$

Figure 1

charge, and limit Li(I) migration. Resolvation of the RCM can cause the protons to leave the octahedral positions [23] 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}, any CEC arising from exchangeable protons would be undetected.

Water adsorption isotherms for Cu (II)-saturated and unexchanged Li(I)-Na(I) forms of RCM are shown in Figure 2. The isotherms reveal two important effects. Firstly, a marked reduction in adsorption occurs with decreasing layer charge for the Cu (II)-saturated forms (Figure 2A). Secondly, the presence of Cu (II) on the exchange sites increases the water adsorption over that of the unexchanged Li(I)-Na(I) RCM with F values of 0.6 and 1.0 (Figure 2B and 2C). The two effects underscore the importance of metal ion hydration in the adsorption process. The enthalpy of hydration of Cu (II) is -2100 kJ $mole^{-1}$, whereas for Li(I) and Na(I) the hydration enthalpies are -579 and -406 kJ $mole^{-1}$, respectively.[24]

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.[19a,b] The low water adsorption isotherms shown in Figure 2B and 2C 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 Å. Since the spacing is not altered appreciably when the minerals are exposed to a free water surface, the possibility of any substantial interlamellar water adsorption is precluded. The presence of collapsed, nonexpandable interlayers also readily accounts for the virtually

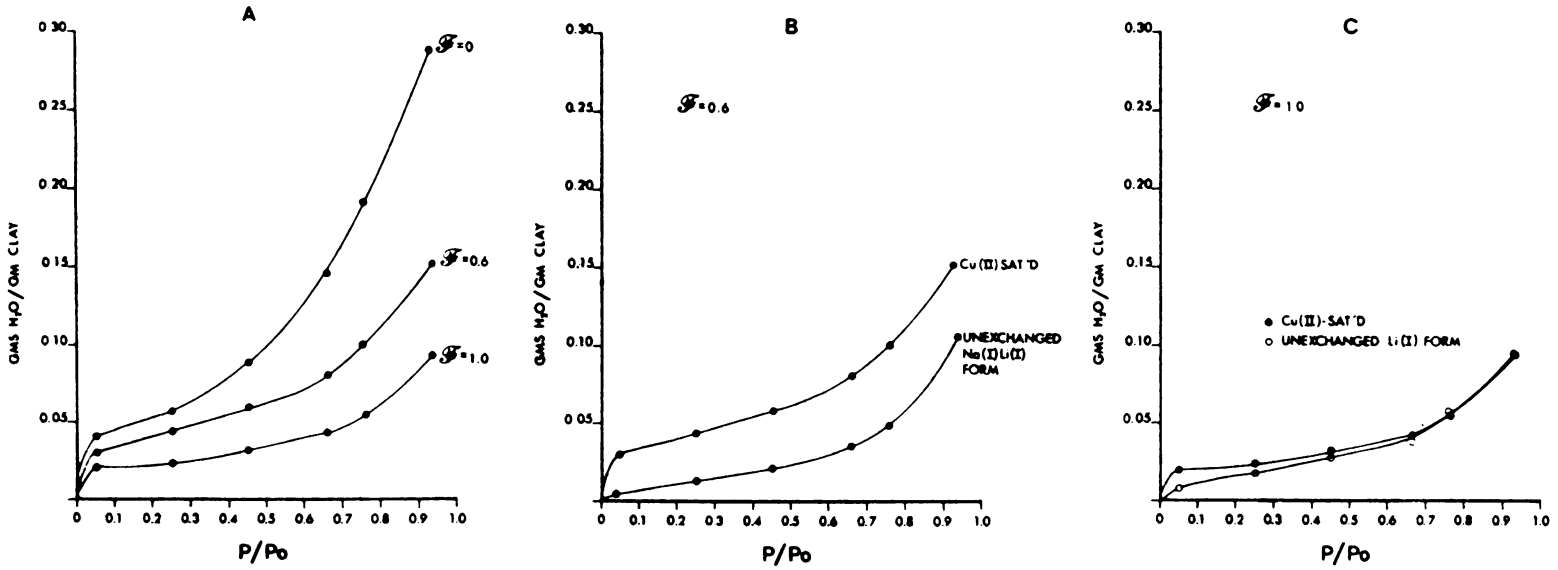

Figure 2. Water adsorption isotherms: A, Cu (II)-saturated RCM having varying amounts of charge reduction; B and C, Cu (II)-exchanged forms of RCM and their unexchanged Na(I), Li(I) counterparts with F values of 0.6 and 1.0, respectively.

identical water adsorption 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 adsorption capacities (cf., Figure 2A). Under air-dried conditions, the broad (001) reflections are centered at 11.6 and 10.4 Å, 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 Å. 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 non-expandable 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 Figure 3A. The low field resonance with $g \simeq 4$ is present in the native mineral and is attributed to iron within the silicate structure.[8c] The hyperfine components of $g_{\perp}$ are unresolved, but those of $g_{\parallel}$ can be distinguished. Perhaps anisotropic effects contribute somewhat to line broadening.[25] 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 Figure 3B. Orientation of the film perpendicular to H gives rise to only the well resolved $A_{\parallel}$ components of $g_{\parallel}$ (Figure 3C). Clearly, the symmetry axis of the aquated

Figure 3. Esr spectra (first derivative representations) for Cu (II)-montmorillonite (RCM, F = 0). A, 4000 Gauss scan of an air-dry, randomly oriented powder sample; B, 1000 Gauss 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.

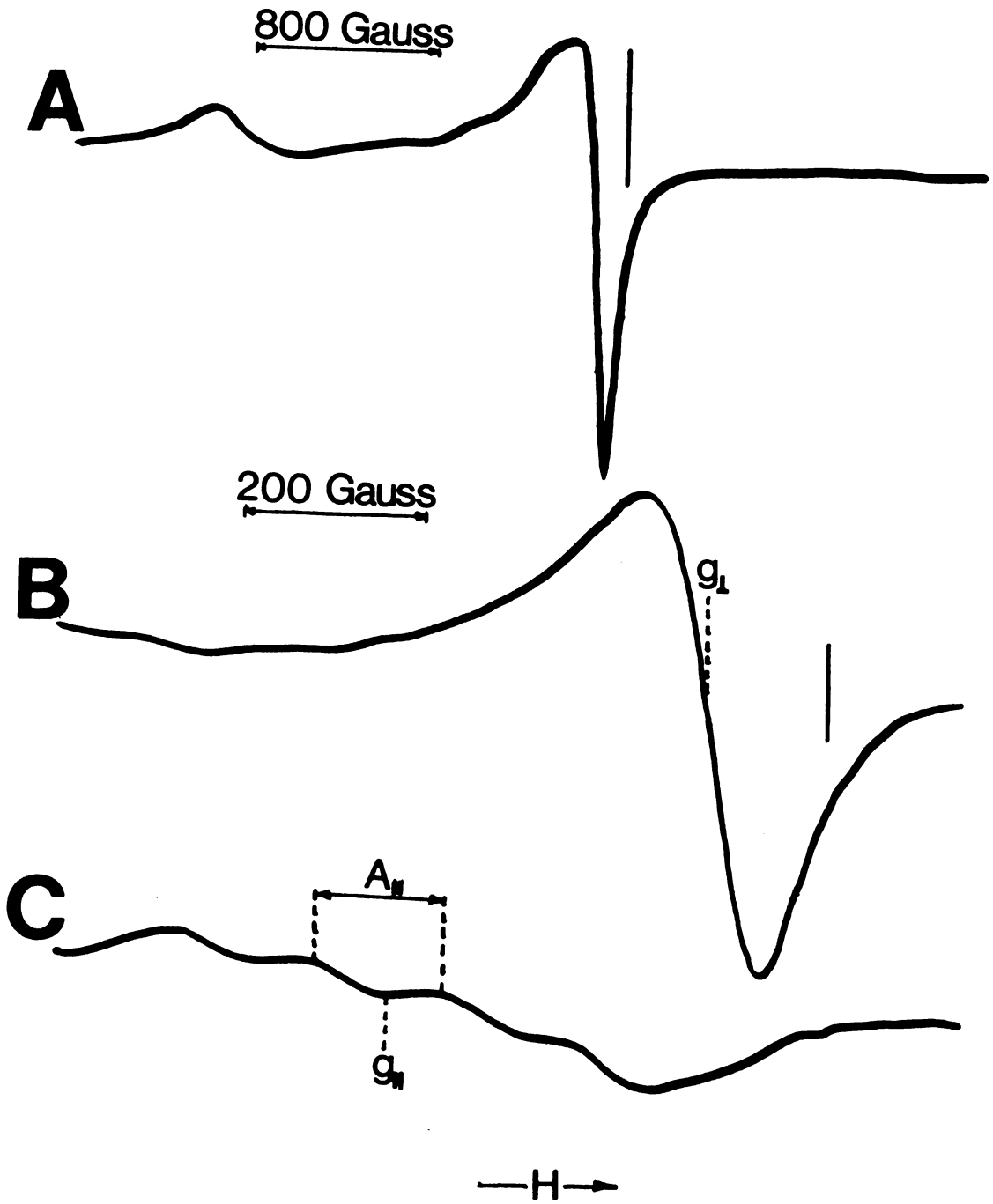

Figure 3

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 esr data for oriented, air-dried samples of Cu (II) RCM.

Table 1. Cation Exchange Capacity and Esr Data for Hydrated Cu (II) Ion on the Surfaces of Reduced Charge Montmorillonites.

F	[Cu(II)] meq/100gm	$g_\perp$ (±0.002)	$\Delta H_\perp$ (Gauss)	$g_\parallel$ (±0.007)	$(10^4)A/C$ (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 esr paramters taken from air-dry, oriented samples at room temperature. Linewidth of the perpendicular component

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 $Cu(H_2O)_4^{2+}$. 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 esr in the presence of $Cu(H_2O)_4^{2+}$. For example, an internally Cu (II)-saturated RCM sample which was heated at 200° for one hour

to drive off coordinated water and allow the Cu (II) ions to occupy sites in hexagonal cavities exhibited a very broad asymmetric line (cf., Figure 5H and I discussed below). Such a weak, broad line would be readily masked by the resonance lines of $Cu(H_2O)_4^{2+}$. Thus, although there may be some layers present which contain Cu (II) in layers devoid of water, especially in those samples with $\underline{F}$ = 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 hours, an intense isotropic Cu (II) signal centered near g = 2.17 appeared. The anisotropic signal characteristic of $Cu(H_2O)_4^{2+}$ was very weak for the samples with $\underline{F}$ = 0.6 and 1.0 and completely absent at $\underline{F}$ = 0.0 and 0.2. The isotropic signal arises because of rapid tumbling or interchange of dynamic Jahn - Teller states for the fully hydrated $Cu(H_2O)_6^{2+}$ ions. [20] Most of the fully hydrated Cu (II) ions at $\underline{F}$ = 0.0 and 0.20 undoubtedly exist in interlayers containing several molecular layers of water, but at $\underline{F}$ = 0.6 and 1.0 a large fraction of the ions probably occupy external exchange sites. It was desirable, therefore, to further elucidate the nature of the external exchange sites on the reduced charge mineral.

The end-member, $\underline{F}$ = 1.0, was selected for detailed investigation. Figure 4A shows the esr 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. [26] Figure 4B shows the powder spectrum of air-dry Cu (II)-saturated RCM at $\underline{F}$ = 1.0. It is obviously unsatisfactory from the standpoint of characterizing the $g_{\parallel}$ component due to the combined effects of sloping baseline and anisotropic broadening. The

Figure 4. ESR spectra of RCM at $\underline{F}$ = 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 hours. Field setting is identical for all samples.

broad hump in the middle of the spectrum can be attributed to a small amount of isotropic Cu (II) in the system. Figures 4C 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 Figure 3 are obtained. The isotropic signal obtained upon exposure to water vapor is illustrated in Figure 4E.

Figures 5A and B are the spectra of a pressed disk of the $\underline{F}$ = 1.0 Li(I)-Na(I) RCM which was washed with $CuCl_2/H_2O$ solutions to replace predominately the external sites with Cu (II) and then air-dried. The spectra are identical to those observed for $Cu(H_2O)_4^{2+}$ in which ions are present both internally and externally (Figure 4). An isotropic signal appears upon exposure of the sample to water (Figure 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 esr 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 [27] with the exception that extreme dehydration

Figure 5. ESR spectra of selectively Cu (II)-saturated RCM ($\underline{F}$ = 1.0) pressed disks: A and B, predomintly 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 one hour, sealed, and allowed to return to room temperature, with H parallel and perpendicular to the silicate layers, respectively.

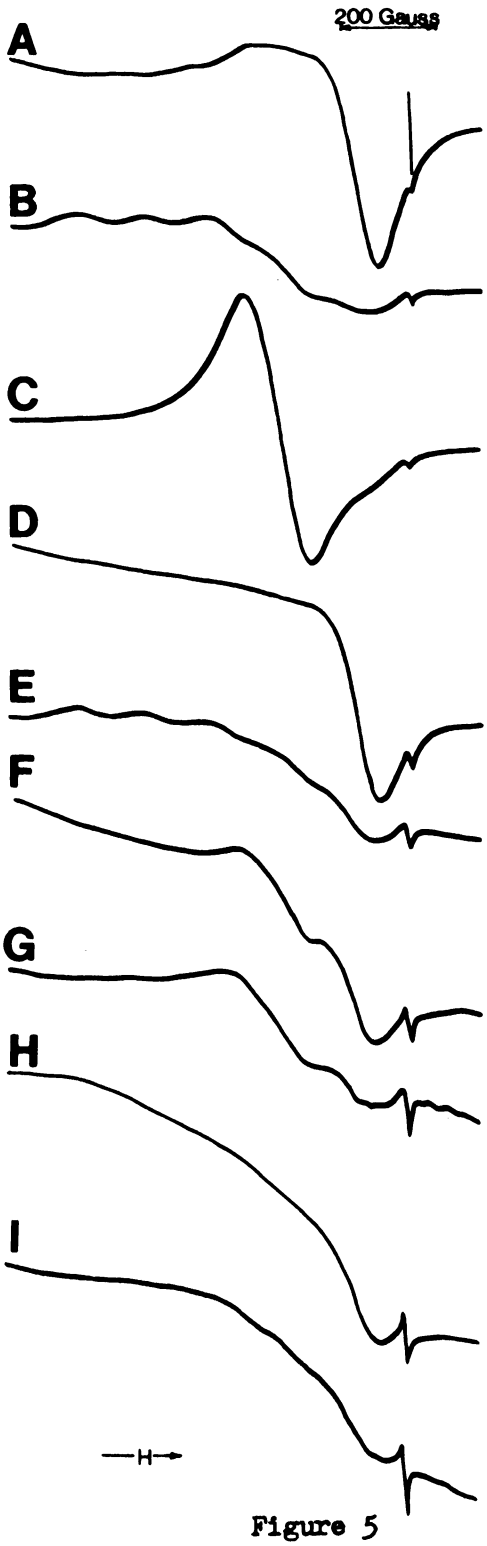

Figure 5

conditions are required to observe an anisotropic signal for the ion on the zeolite surface.

Preferential internal Cu (II) exchange was accomplished by replacing external Cu (II) sites of totally Cu (II)-saturated $\underline{F}$ = 1.0 RCM with tetrabutylammonium ion. Under air-dried conditions the esr signal is orientation dependent and indicative of the tetraaquo species (Figure 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 $Cu(H_2O)_4^{2+}$, 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 (Figure 5F and G) there is some indication of isotropic Cu (II), probably present in layers that can expand. The loss of the $A_{||}$ components of $g_{||}$ for the tetraaquo 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 Figure 5H 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 esr in the presence of $Cu(H_2O)_4^{2+}$.

In order to verify that selective Cu (II) saturation on internal and external sites was achieved for the $\underline{F}$ = 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% 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 expandable by water in the initial Li(I)-RCM at $\underline{F}$ = 1.0 would lead to an over estimate of the external Cu (II) CEC. On the other hand, expandable interlayers in the corresponding Cu (II) RCM would cause the internal CEC to be under estimated. 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 $\underline{F}$ = 0.6 where there is a greater degree of interstratification and a larger number of water -expandable interlayers. The percent deviation for the sum of apparent internal and external CEC is more than twice that obtained at $\underline{F}$ = 1.0.

If we attribute the deviation for the sum of internal and external Cu (II) CEC at $\underline{F}$ = 1.0 to an over estimate of the number of external sites, then the external CEC is 20 meq/100 gm. An identical CEC was obtained by Brindley and Ertem [19b] for NH_4^+ exchange of Li(I) RCM at $\underline{F}$ = 1.0, and this value probably is also an accurate estimate of the external CEC. It has been previously estimated that approximately 20% of the total CEC of montmorillonite is due to the presence of external sites.[28] Therefore, it is somewhat surprising that the

external CEC of RCM at $\underline{F} = 1.0$ 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 solvated. Further studies are needed, however, to test this latter hypothesis.

Table 2. Cation Exchange Data Obtained by Conductometric Titration of Selectively Cu (II)-Saturated RCM's

Sample	Primary Type of Exchange Site	[Cu(II)] meq/100gm	Sum of Internal and External CEC	% Deviation
$\underline{F} = 1.0$	Total CEC	27		
	External	22	29	7
	Internal	7		
$\underline{F} = 0.6$	Total CEC	53		
	External	28	65	18
	Internal	37		

SUMMARY AND CONCLUSIONS

The nature of hydrated Cu (II) ions in 2:1 layer silicates can be depicted as follows. When the expanding minerals of the montmorillonite type are in aqueous suspension, the individual layers within a tactoid are separated by a distance of approximately 10 Å. - Under this condition the ion exists as a hexaaquocopper (II) complex and tumbles rapidly in the interlamellar space. Alternatively, in the vermiculite-like minerals where interlamellar expansion is limited to two molecular layers of water (ca. 4 Å), the ion exists as hexaaquocopper (II) but is restricted with its symmetry axis inclined approximately 45° to the silicate sheets. In either case, partial dehydration removes water from the interlayer until a monolayer remains. Under this condition the ion preferentially loses its two axial water molecules and coordinates to opposite surfaces of the silicate layers as the tetraaquo species along the c-axis. This reaction is reversible and rehydration facilitates a return to the hexaaquo species which is restricted in vermicullite but rapidly tumbles in montmorillonite.

These observations have been useful in revealing several important features of reduced charge montmorillonite. Regardless of the amount of charge reduction, complete 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 $\underline{F}$ = 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 ($\underline{F}$ = 1.0) approximately 75% of the copper ions occupy <u>external</u> 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 $Cu(H_2O)_4^{2+}$, 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 $Cu(H_2O)_6^{2+}$ and tumble rapidly. The $Cu(H_2O)_4^{2+}$ 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 hetergeneity 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).

BIBLIOGRAPHY

BIBLIOGRAPHY

1. H. E. Doner and M. M. Mortland, Science, 166, 1406 (1969).

2. M. M. Mortland and T. J. Pinnavaia, Nature Phys. Sci., 229 75 (1971).

3. T. J. Pinnavaia and M. M. Mortland, J. Phys. Chem., 75, 3957 (1971).

4. D. B. Fenn and M. M. Mortland, Proc. Int. Clay Conf., Madrid, June, 1972.

5. J. P. Rupert, J. Phys. Chem., 77, 784 (1973).

6. R. Cohen and C. Heitner-Wirguin, Inorg. Chim. Acta., 3, 647 (1969); R. J. Faber and M. T. Rogers, J. Amer. Chem. Soc., 81, 1849 (1959); C. Heitner-Wirguin and R. Cohen, J. Phys. Chem., 71, 2556 (1967); K. Umezawa and T. Yamabe, Bull. Chem. Soc. Japan, 45, 56 (1972).

7. J. T. Richardson, J. Catalysis, 9, 178 (1967); J. Turkevich, Y. Ono and J. Soria, ibid., 25, 44 (1972).

8. (a) A. Furuhata and K. Kuwata, Nendo Kagaku, 19 (1969); (CA 72: 105744). (b) Y. I. Taracevich and F. D. Ovcharenko, Proc. Int. Clay Conf., Madrid, 1972. (c) B. R. Angel and P. L. Hall, Proc. Int. Clay Conf., Madrid, 1972.

9. I. V. Matyash, Geochem. Int., 6, 676 (1967).

10. R. C. Kemp, J. Physics, 4, L11 (1971).

11. V. C. Farmer and J. D. Russell, Trans. Farad. Soc., 67, 2737 (1971).

12. J. E. Wertz and J. R. Botton, "Electron Spin Resonance", McGraw Hill, Inc., New York, New York, 1972, p. 287.

13. L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1960.

14. G. F. Walker, Clays and Clay Minerals, 4, 101 (1956).

15. S. Fujiwara, S. Katsumata, and T. Seki, J. Phys. Chem., 71, 116 (1967).

16. B. R. McGarvey in "Transition Metal Chemistry", Vol. 3, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, (1966).

17. A Hudson, Mol. Phys., 10, 575 (1966).

18. S. Fujiwara and H. Hayashi, J. Chem. Phys., 43, 23 (1965).

19. (a) R. Calvet and R. Prost, Clays and Clay Minerals, 19, 175 (1971).
(b) G. W. Brindley and G. Ertem, Clays and Clay Minerals, 19, 399 (1971).
(c) G. Ertem, Clays and Clay Minerals, 20, 199 (1972).

20. D. M. Clementz, "The Nature of Hydrated Copper (II) Ions in Layer Silicates" Part I. Ph.D. Thesis, Michigan State University, (1973).

21. M. M. Mortland and J. L. Mellor, Soil Sci. Soc. Am. Proc. 18, 363 (1954).

22. V. C. Farmer, and J. D. Russell, Clays and Clay Minerals, 15, 121 (1967).

23. M. M. Mortland, Clay Minerals, 6, 143 (1966).

24. F. A. Cotton and G. F. Wilkinson, "Advanced Inorganic Chemistry" 3rd ed., John Wiley and Sons, New York, 645 (1972).

25. F. J. Adrian, J. Colloid & Int. Sci, 26, 317 (1968).

26. H. Z. Friedlander, C. R. Frink, and J. Saldick, Nature 199, 61 (1963); R. D. Wauchope and R. Haque, Nature (Phys. Sci.), 233, 141 (1971).

27. J. Turkevich, Y. Ono, and J. Soria, J. Catalysis, 25, 44 (1972).

28. R. E. Grim, "Clay Minerology", 2nd ed., McGraw Hill (1968).