CHEMISORPTION OF Cu(II) AND Co(II) ON ALLOPHANE AND IMOGOLITE

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Abstract—Adsorption of Cu^{2+} and Co^{2+} by synthetic imogolite, synthetic allophanes with a range of SiO_2/Al_2O_3 ratios, and allophanic clay fractions from volcanic ash soils was measured in an ionic medium of 0.05 M $Ca(NO_3)_2$. The effect of pH (and metal concentration) on adsorption was qualitatively similar for the synthetic and natural allophanes with relatively minor changes in behavior caused by variable SiO_2/Al_2O_3 ratios. Cu and Co were chemisorbed by allophane at pH 5.0–5.5 and 6.9–7.2 (pH values for 50% adsorption level), respectively, with concomitant release of 1.6–1.9 protons/metal ion adsorbed. Quantitatively, adsorption by imogolite was less than that by the allophanes, presumably because of fewer sites available for chemisorption on the tubular structure of imogolite. Electron spin resonance studies of the imogolite and allophanes revealed that Cu^{2+} was adsorbed as a monomer on two types of surface sites. The preferred sites were likely adjacent AlOH groups binding Cu^{2+} by a binuclear mechanism; weaker bonding occurred at isolated AlOH or SiOH groups. These chemisorbed forms of Cu^{2+} were readily extracted by EDTA, CH_3COOH, and metals capable of specific adsorption, but were not exchangeable. In addition, the H_2O and/or OH^- ligands of chemisorbed Cu^{2+} were readily displaced by NH_3, with the formation of ternary Cu-ammonia-surface complexes.

Key Words—Allophane, Chemisorption, Cobalt, Copper, Electron spin resonance, Imogolite, SiO_2/Al_2O_3.

INTRODUCTION

The observation that certain heavy metal cations tend to adsorb specifically on hydrous oxide and ox-yhydroxide surfaces (Kinniburgh *et al.,* 1976; Forbes *et al.,* 1976; McKenzie, 1980) suggests that these minerals play a significant role in the retention of trace metals by soils. Similarly, high surface-area alumino-silicates, such as allophane and imogolite, should be active metal adsorbents. The ability of Andisols to adsorb heavy metals specifically has been demonstrated by Forbes (1976) and Abd-Elfattah and Wada (1981); however, no systematic study has determined the effect of allophanic composition on adsorption (Henmi and Wada, 1976) or those parameters important to specific adsorption (pH and solution metal concentration) using clay separates from these soils.

The specific adsorption of Cu and Co by allophane and imogolite is evaluated in this paper using a series of clays and their synthetic analogues. Use of the latter materials avoided interference from other hydrous metal oxides and organic matter and, additionally, allowed the ligand field properties of bound Cu to be probed using electron spin resonance (ESR).

MATERIALS AND METHODS

The isolation and characterization of the natural samples has been described elsewhere (Clark and McBride, 1984). Allophanic clay fractions (<2 μm) from three field-moist volcanic ash soils, Egmont (Eg),

Te Akatea (Te Ak), and Kakino (KnP), have SiO_2/Al_2O_3 (SA) ratios of 0.95, 1.51, and 1.92. Synthetic allophanes with SiO_2/Al_2O_3 ratios of 1.10, 1.34, 1.67 and synthetic imogolite were prepared and characterized as before (Clark and McBride, 1984). Dry samples were used throughout, and all results are expressed on a 150°C oven-dry clay basis.

Adsorption experiments were carried out in 50-ml stoppered polypropylene centrifuge tubes, with suspensions containing 100 mg of material in 20 ml of 0.05 M $Ca(NO_3)_2$. No attempt was made to exclude dissolved CO_2. Tubes were shaken for 24 hr to allow surface rehydration and saturation of the exchange sites with Ca^{2+} and NO_3^-. Following centrifugation, the aqueous phase was discarded, and the samples were resuspended in 0.05 M $Ca(NO_3)_2$ containing concentrations of Cu and Co between 10^{-5} and 10^{-3} M. The suspensions were shaken for a further 24-hr period and the pH adjusted periodically to predetermined values. Adjustments using 0.1 M HNO_3 and saturated $Ca(OH)_2$ caused, in all experiments, $<5\%$ change of the initial 20-ml volume, and corrections for the quantity of metal present in the final solution were made accordingly. After equilibration, Cu and Co were determined in centrifuged supernatants, Cu by atomic absorption spectroscopy and Co colorimetrically after complexation with 1-(2-pyridylazo)-resorcinol (Busev and Ivanov, 1963). Adsorbed metal was calculated by difference, and equated to the quantity of metal chemisorbed, inasmuch as electrostatic adsorption of Cu^{2+} and Co^{2+} should have been almost completely suppressed by the presence of excess Ca^{2+}.

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At the conclusion of the adsorption experiments, all synthetic Cu-containing samples were centrifuge-washed 3 times with 10 ml of distilled water and the wet gels sampled in a capillary tube for ESR analysis with a Varian E-104 (x-band) spectrometer. Alternatively, powder spectra were obtained using 50 mg of air-dried samples in quartz tubes. The lability of sorbed Cu was assessed by remoistening the air-dried powders with several drops of water and exposing them to ammonia vapor overnight prior to further spectral analysis. ESR spectra of all samples were determined at room temperature and for selected samples at lower temperature with the Varian E-257 variable temperature accessory.

Hydrogen ions released during metal adsorption were measured by titrating suspensions of Te Akatea or sample SA 1.10 with 0.004 M NaOH, pH control being maintained by a Chemtrix pH Controller Type 45AR and a coupled peristaltic pump. Surface rehydration and pH adjustment to 6.0 (Cu) or 7.5 (Co) commenced several days prior to metal addition in an attempt to minimize other surface reactions. At the conclusion of this pre-equilibrium period, the centrifuged supernatants were removed and the suspensions were prepared in triplicate containing 200 mg of sample and 5×10^{-4} M Cu^{2+} or Co^{2+} in 20 ml of 0.05 M $Ca(NO_3)_2$. Preliminary experiments established that the metal adsorption reaction was rapid and essentially complete within 3 hr; hence, a titration period of 10 hr was selected with pH maintained at a constant value throughout. Blank titrations were performed with samples that had received identical pretreatments, and the difference in titrimetric volume for systems with and without trace metal was attributed to neutralization of protons released on adsorption. Bicarbonate buffering was minimized by freshly preparing solutions in CO_2-free distilled water and simultaneously passing pure, humidified N_2 through the suspension.

The extractability of chemisorbed species was determined using the SA 1.34 allophane with either 0.01 M $CaCl_2$, 0.4 M acetic acid, 0.05 M EDTA neutralized to pH 7 with NH_3 (after Jarvis, 1981), or 0.05 M $Pb(NO_3)_2$. A single 2-hr extraction period and sample/solution ratio of 1:10 was used in each experiment.

RESULTS AND DISCUSSIONS

Adsorption as a function of pH and concentration

The appearance of adsorption edges for Cu at lower pH than those for Co (Figures 1 and 2) are consistent with the general relationship between metal affinity for surfaces and tendency to hydrolyze (Elliot and Huang, 1979; Kinniburgh et al., 1976). The sorption of positively charged metal species in the presence of 0.05 M Ca^{2+} onto a positive surface, the shift of adsorption edges towards higher pH as metal ion concentration increases (Figure 3), and undersaturation with respect
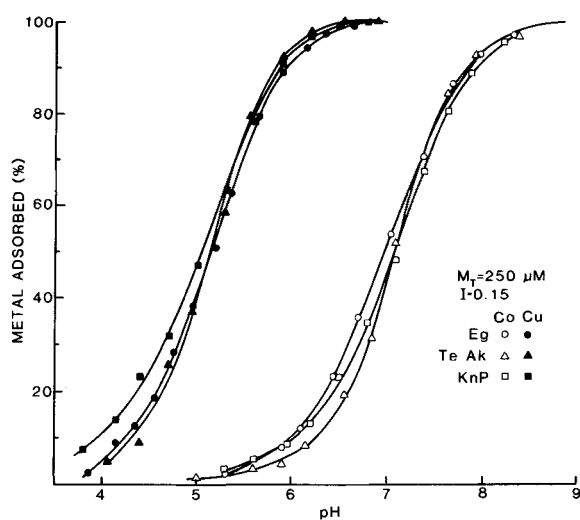

Figure 1. Adsorption of Cu^{2+} and Co^{2+} by allophanic clays as a function of pH from a 0.05 M $Ca(NO_3)_2$ solution containing 2.5×10^{-4} M metal. The symbol I refers to the ionic strength of the solution.

to the least soluble hydroxide or hydroxycarbonate phase (Figure 4) all indicate that Cu and Co were specifically adsorbed by allophane and imogolite.

Because it had been generally observed that adsorption, hydrolysis, and precipitation occur over a narrow pH range (James and Healy, 1972), Elliot and Huang (1979) suggested that surface-induced precipitation of a separate sorbate phase or adsorption of multinuclear hydrolysis products may occur. Inasmuch as a linear relationship was established between the Cu^{2+} ESR signal intensity and the quantity of "adsorbed" copper with all synthetic samples (see ESR section), the ad-
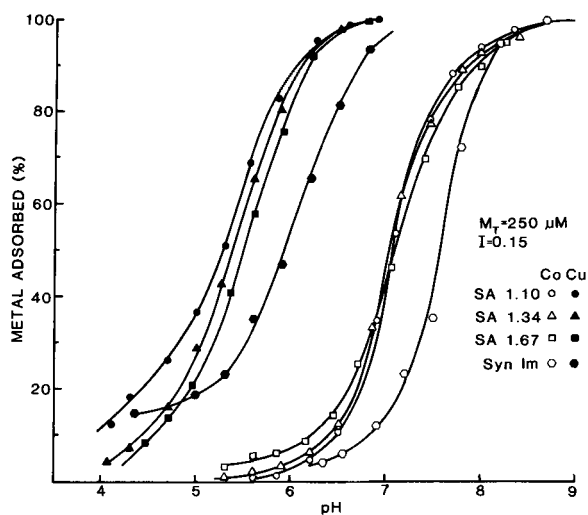

Figure 2. Adsorption of Cu^{2+} and Co^{2+} by synthetic allophane and imogolite as a function of pH from a 0.05 M $Ca(NO_3)_2$ solution containing 2.5×10^{-4} M metal.
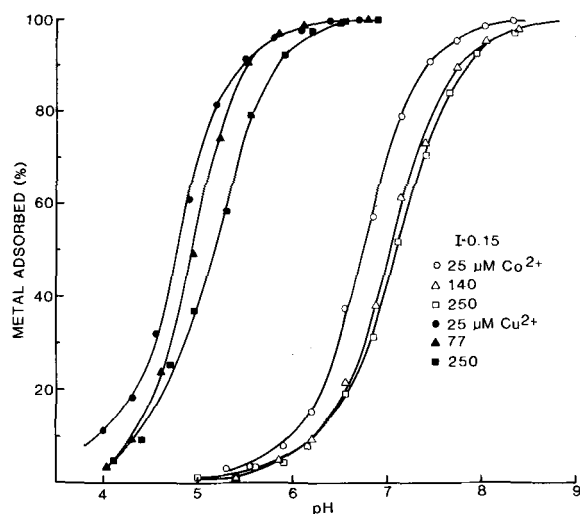
Figure 3. Adsorption of Cu^{2+} and Co^{2+} by Te Akatea allophanic clay as a function of pH and metal concentration from a 0.05 M $Ca(NO_3)_2$ solution.

sorption of monomeric, rather than polymeric hydroxy species is indicated. The highest trace metal loading achieved, 130 mmole Cu/kg, represents an approximate average Cu–Cu separation of 34 Å at the surface, a distance sufficiently large to explain the absence of dipolar broadening in the ESR spectra.

With the exception of Cu adsorption on synthetic allophane, where retention at a given pH increased with alumina content (Figure 2), composition was a relatively ineffective parameter in controlling sorption predictably over the range of metal concentrations used here. The pH at which 50% retention (pH_{50}) occurred varied slightly with the SA ratio (Figures 1 and 2), Cu between 5.0 and 5.25 for allophanic clays, with corresponding values of 5.25–5.50 for the synthetic analogues, and Co between 6.95 and 7.15 for all samples. Lower Cu pH_{50} values for soil clays can be attributed to previous sorption events in soil with organic matter or phosphate anions. The differences exhibited by freshly formed allophanic surfaces, then, were likely transient because in dynamic soil environments they would have been nullified by various adsorption or precipitation processes. The unpredictable effect of composition is further substantiated by the adsorption isotherms in Figures 5 and 6, where adsorption maxima vary marginally on the synthetics and more extensively with the soil clay systems.

Trace metal adsorption on imogolite was markedly lower than that on allophane (Figures 5 and 6). The appearance of an adsorption plateau for imogolite between pH 4 and 5 of 10–12 mmole Cu/kg (Figure 2) is atypical when compared with data for Al and Fe gels (Kinniburgh *et al.*, 1976) or with the allophanic samples in Figures 1 and 2. It is possible that intercalation (physical adsorption into micropores) of uncharged cupric nitrate ion-pairs took place, for, although the Ca^{2+}
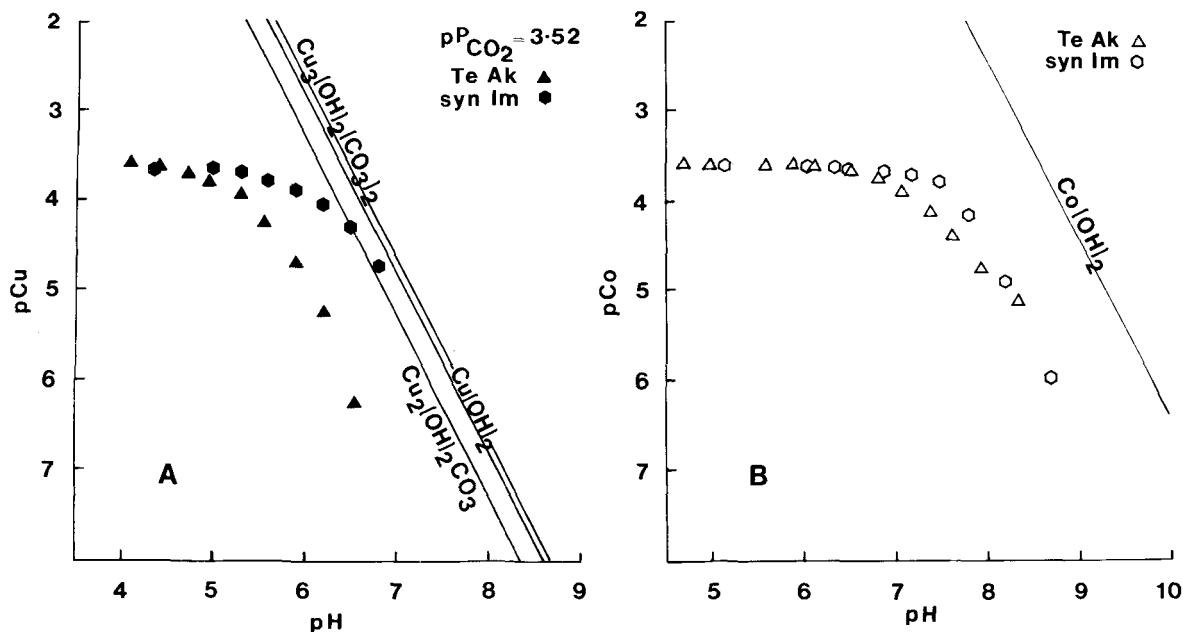

Figure 4. Solubility of Cu and Co (plotted as pM = −log (M^{2+})) after 24-hr equilibration of Te Akatea clay and synthetic imogolite in (A) 2.5 × 10⁻⁴ M Cu in 0.05 M $Ca(NO_3)_2$, and (B) 2.5 × 10⁻⁴ M Co in 0.05 M $Ca(NO_3)_2$. Solubility lines for copper hydroxide, malachite, and azurite were determined from the data of Lindsay (1979), and cobalt hydroxide from those of Baes and Mesmer (1976), assuming atmospheric partial pressure of CO_2 (−log P_{CO_2} = 3.52).
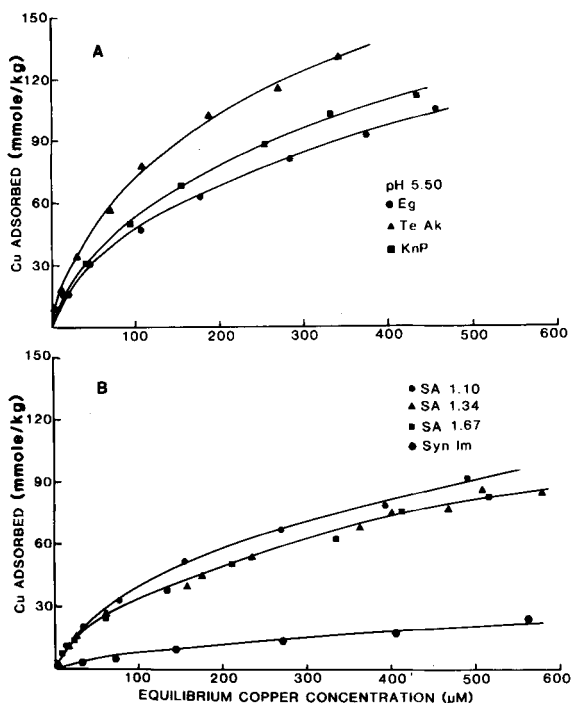
Figure 5.   Isotherms for adsorption of Cu^{2+} from a 0.05 M $Ca(NO_3)_2$ solution on (A) allophanic soil clays, and (B) synthetic allophane or imogolite.
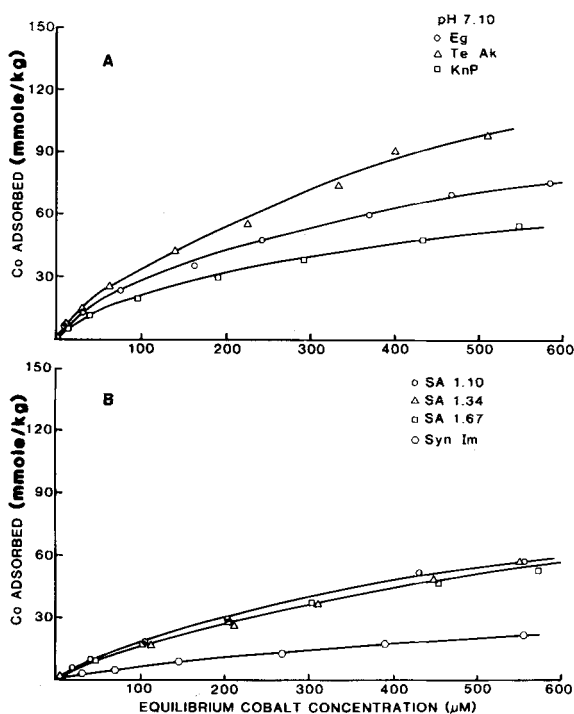

Figure 6.   Isotherms for adsorption of Co^{2+} from a 0.05 M $Ca(NO_3)_2$ solution on (A) allophanic soil clays, and (B) synthetic allophane or imogolite.
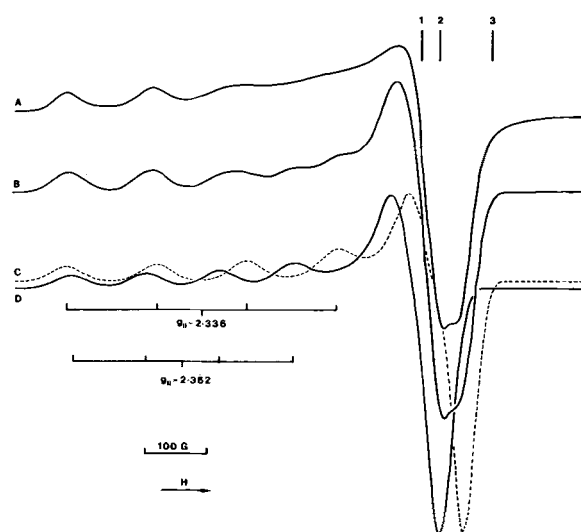

Figure 7.   Actual (A) and simulated (B) electron spin resonance spectrum at 22°C of Cu^{2+} adsorbed on sample SA 1.10 at pH 6.0. Two computer-generated spectra of Cu^{2+}, (C) and (D), were used to construct the simulated (B) spectrum. The numbered vertical lines represent the $g_\perp$ resonance positions at 2.075 (1) and 2.056 (2), and the free electron field position at 2.0023 (3).

concentration exceeded that of Cu^{2+} by more than 2 orders of magnitude over this pH range, the stability constants for $CuNO_3^+$ and $Cu(NO_3)_2^0$ were sufficiently high relative to those for the respective calcium species to ensure that Cu complexes existed in solution. The lack of evidence for Co intercalation may reflect the low stability of aqueous cobalt nitrate complexes.

Based on the amount of "active" Al–OH in imogolite, 100 mmole/kg (Clark and McBride, 1984), combined with assumptions of a 13-Å external radius and 28 edge-sorption sites/tubule (Farmer and Fraser, 1978), Co and Cu adsorption of ~30 mmole/kg (Figures 5B and 6B) represents 8 ions/tube, or an average inter-metal separation of 20 Å for ions on terminal edge sites. Although the solubility product of malachite $(Cu_2(OH)_2CO_3)$ was exceeded at the highest pHs (Figure 4), the ESR evidence (see below) suggests that all adsorbed Cu^{2+} was bound in a monomeric form at well-separated surface sites.

Electron spin resonance of adsorbed Cu on allophane and imogolite

Irrespective of SA ratio, pH, and metal-uptake level, rigid-limit spectra typical of immobilized Cu species were observed for both air-dry and wet synthetic allophanes (Figure 7A). Of the 4 low-field $g_\parallel$ resonances arising from interaction between the unpaired electron spin and I = 3/2 nuclear spin, only 3 could be cleanly resolved; the fourth was concealed beneath the $g_\perp$ shoulder. The asymmetry and broadening of $g_\parallel$ resonances (especially toward higher field) and the
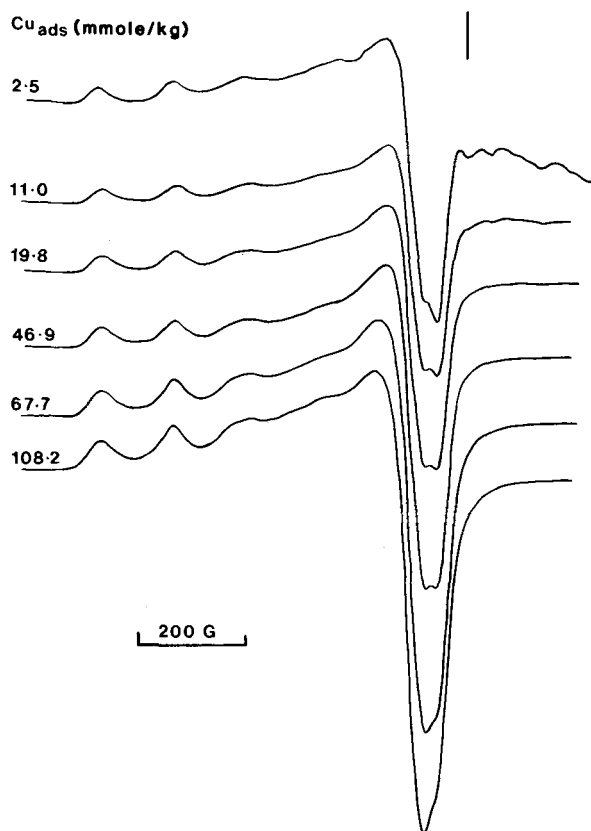
Figure 8. Electron spin resonance spectra of Cu^{2+} chemisorbed over a range of concentrations at pH 5.50 by synthetic (SA 1.10) allophane. The vertical line in this, and subsequent illustrations, marks the free electron position.

Figure 9. Electron spin resonance spectra of Cu^{2+} chemisorbed at pH 5.50 by soil clays.

presence of two high-field $g_\perp$ components is indicative of Cu immobilized in two distinct environments. The ESR parameters for each rigid-limit species were estimated using computer simulation (Table 1). A typical reconstructed spectrum and its two resolved components are shown in Figures 7B, 7C, and 7D, respectively.

From the spectral parameters for $Cu(H_2O)_6^{2+}$ and $Cu(OH)_4^{2-}$ listed in Table 1, it is evident that the replacement of equatorial H_2O ligands by OH^- caused decreased $g_\parallel$ and larger $A_\parallel$ values. Therefore, the more intense spectrum ($g_\parallel = 2.336$) may have been the result of sorption of Cu species where two ligand H_2O molecules were replaced by oxygens or hydroxyls and coordination to the surface was by a bi-nuclear mechanism. The site geometries hypothesized for Cu adsorbed on noncrystalline alumina (McBride, 1982) are appropriate here because comparable $Al(OH)H_2O$ groups present at edges or "defects" in the structure were the probable binding sites. The weaker spectrum ($g_\parallel = 2.362$) may be attributed to Cu^{2+} bound by a second mechanism, possibly to an AlOH or SiOH group.

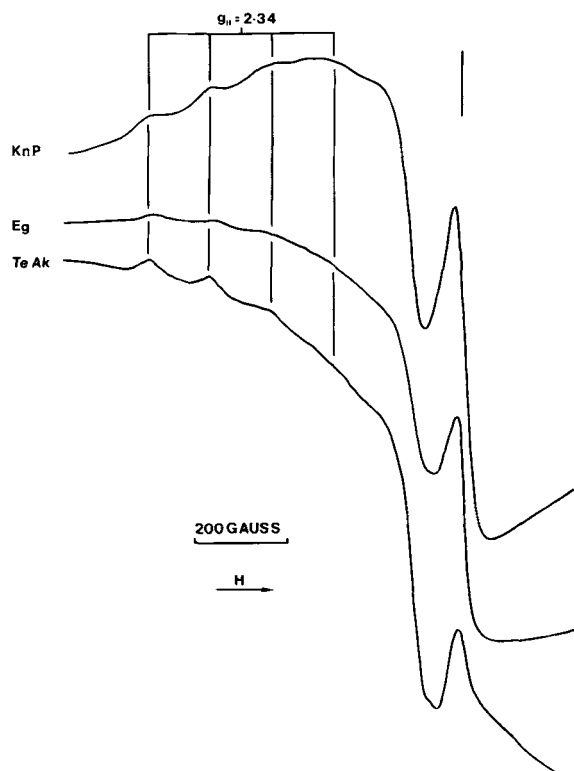Whereas spectral parameters remained unaltered at different levels of specific adsorption at a given pH, the relative intensity of the two Cu^{2+} spectra changed, indicating a shift in the distribution of Cu between the two sites. The distribution is dependent both on the amount of sorbed metal and SA ratio. Sample SA 1.10 demonstrated the greatest variation (Figure 8). At lowest retention, the high field $g_\perp$ resonance was more intense. As the amount of adsorbed metal increased, the low-field component equalled, then surpassed the other. The low-field resonance equalled (for SA 1.34) or surpassed (for SA 1.67) the intensity of the high-field resonance at the lowest levels of adsorption and increased further with additional adsorbed Cu.

With other variables constant, the effect of pH on the ESR spectra was similar to the effect of adsorbate concentration, because its primary effect was to increase specific adsorption. For adsorption of 50 mmole Cu^{2+}/kg over the pH range 4–7 (shown in Figure 2), the low-field $g_\perp$ components predominated for the high-silica allophanes. For the low-silica allophane (SA = 1.10), the relative $g_\perp$ intensities equalized at pH 5.30, with the low-field signal favored at higher pH and the high-field signal favored at lower pH.

The measured proton release upon Cu adsorption for sample SA 1.10 at pH 6 was 1.6 per Cu^{2+} ion, providing further evidence in addition to the ESR spec-
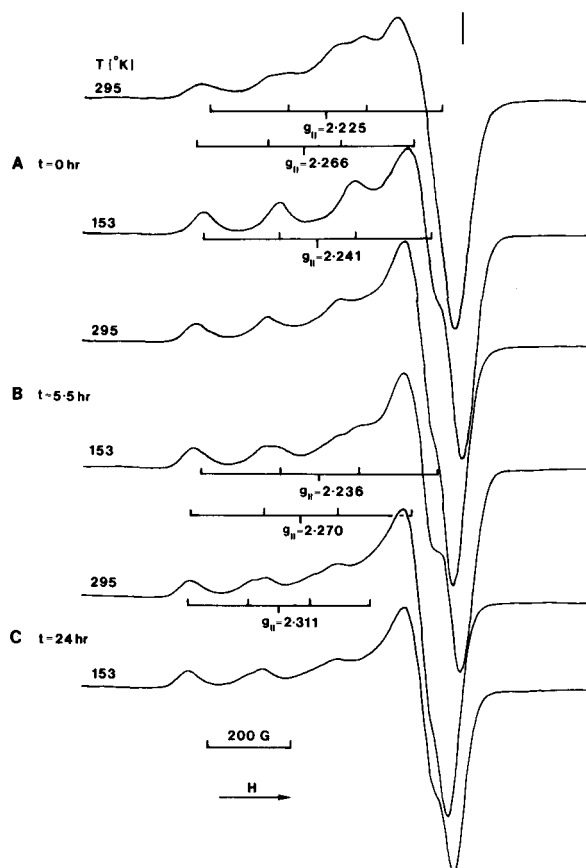
Figure 10.   Electron spin resonance spectra at 22 and −120°C of Cu²⁺ adsorbed at pH 5.50 on allophane (SA 1.10) after exposure to NH₃ vapor for 1 day. The spectra were recorded immediately (A), 5.5 hr (B), and 24 hr (C) after removal from NH₃. The Cu²⁺ adsorption level on the allophane was 92 mmole/kg.

tra that Cu^{2+} bonding may have involved more than a single mechanism. The experimental proton release for Te Akatea clay was 1.9 per Cu ion; however, although a rigid-limit spectrum imposed on a broad g =

2 ferromagnetic signal was visible (Figure 9), insufficient detail was present to attempt a simulation. Nevertheless, the $g_{\perp}$ component was consistent with the high-field Cu^{2+} signal. Proton release ratios of 1.6 and 1.8 were similarly measured at pH 7.5 for Co adsorption on samples SA 1.10 and Te Akatea, respectively.

No additional features beyond those used for the allophanes are necessary to describe the spectral characteristics of Cu adsorbed on imogolite. Two sites, with parameters very similar to those of allophane (Table 1), adequately simulate the ESR spectra. Response of the imogolite spectra to pH and Cu^{2+} concentration was similar to that of the SA 1.67 allophane, with the signal having high g values always more intense than the signal having low g values.

The ESR spectrum with low g-values was undoubtedly due to Cu^{2+} chemisorbed at AlOH sites, possibly by a binuclear mechanism with the release of 2 protons. The similarity of this spectrum to one observed for Cu^{2+} adsorbed on noncrystalline aluminum hydroxide (McBride, 1982) and the low pH at which this signal appears are evidence in support of this assignment. The second spectrum with high g-values is less clearly assigned. A spectrum with similar parameters was observed for aluminum hydroxides (McBride, 1982), but experiments with silica gels showed the appearance of rigid-limit Cu^{2+} ESR spectra at pHs as low as 4 (von Zelewsky and Bemtgen, 1982), indicating that Cu^{2+} can chemisorb on silanol groups at the pHs used in the present study. The spectral parameters for Cu^{2+} adsorbed on wet, noncrystalline silica at pH 6.7 were $g_{\parallel} = 2.37$, $g_{\perp} = 2.085$, $A_{\parallel} = 125 \times 10^{-4}$ cm⁻¹, not unlike the parameters reported in Table 1 for the second adsorption site on allophane and imogolite. On drying the silica, these parameters shift to $g_{\parallel} = 2.36$, $g_{\perp} = 2.05$, $A_{\parallel} = 138 \times 10^{-4}$ cm⁻¹.

Given that the spectral parameters for Cu^{2+} adsorbed on silica are similar to those for Cu^{2+} bound on one site of the allophane and imogolite (Table 1), it is reasonable to assign the spectrum with high g-values to

Table 1.   Electron spin resonance parameters of adsorbed Cu(II)-hydroxy complexes.

System	T (°C)	g∥	g⊥	A∥ (cm⁻¹)	Reference
$Cu(H_2O)_6^{2+}$-water-glycerol	20	2.409	2.082	0.0144	Bassetti *et al.* (1979)
$Cu(OH)_4^{2-}$-water-NaOH	−196	2.261	—	0.0186	Ottaviani and Martini (1980)
Cu(II)-silica gel (pH 7)[1]	25	2.380	2.085	0.0128	von Zelewsky and Bemtgen (1982)
Cu(II)-alumina	20	2.332	—	0.0144	Bassetti *et al.* (1979)
Cu(II)-imogolite	22	2.336	2.065[2]	0.0156	This study
		2.362	2.082[2]	0.0129	
Cu(II)-allophane	22	2.336	2.056[2]	0.0156	This study
		2.362	2.075[2]	0.0129	
Cu(II)-noncrystalline alumina	22	2.32	2.07	0.0168	McBride (1982)
		2.37	2.08	0.0138	
Cu(II)-boehmite	22	2.36	2.07	0.0143	McBride (1982)

[1] Parameters were determined using a moist "Aerosil 300" suspension.
[2] Determined by computer simulation. A⊥ is estimated to be approximately 0.0015 cm⁻¹.

Table 2. Electron spin resonance parameters of adsorbed copper(II)-ammonia complexes.

System	T (°C)	$g\parallel$	$g\perp$	$A\parallel$ (cm^{-1})	Reference
$Cu(NH_3)_4(H_2O)_2^{2+}$-H_2O-NH_3	−196	2.245	2.061	0.0192	Vierke (1971)
$Cu(NH_3)_5H_2O^{2+}$-H_2O-NH_3	−196	2.245	2.046	0.0182	Martini *et al.* (1980)
$Cu(NH_3)_5H_2O^{2+}$-alumina	20	2.267	2.062	0.0190	Martini *et al.* (1980)
		2.315	—	0.0167	
	−196	2.277	2.051	0.0194	
$Cu(NH_3)_5H_2O^{2+}$-silica	20	2.229	2.034	0.0187	Martini and Bassetti (1979)
	−196	2.243	2.048	0.0196	
$Cu(NH_3)_4^{2+}$-zeolite	−105	2.235	—	0.0186	Vedrine *et al.* (1974)
Cu-NH$_3$-allophane	22	2.225	—	0.0192	This study
		2.266	—	0.0182	
		2.311	—	0.0151	
	−120	2.236	—	0.0196	
		2.241	—	0.0188	
		2.270	—	0.0185	
Cu-NH$_3$-imogolite	22	isotropic spectrum g_o = 2.120, A_o = 0.0082			
		2.266		0.0185	
		2.320	—	0.0141	
	−120	2.228	—	0.0216	
		2.272	—	0.0186	

Cu^{2+} bound to SiOH groups. In support of this hypothesis is the fact that the higher g-values for Cu^{2+} intensify (1) at high pH, (2) at higher levels of adsorption, and (3) with the allophanes having higher silica/alumina ratios. Such results are to be expected if the energetically favored sites of adsorption were AlOH groups, with only minor adsorption at SiOH groups until the preferred sites were occupied. The high g-values suggest that Cu^{2+} may have bonded to a single Si–OH group via an axial ligand position, retaining its equatorial ligand water. The result would have been the displacement of a single proton into solution, consistent with the observed proton-release data which show that 1–2 protons were released for each Cu^{2+} ion chemisorbed on allophane. Because SiOH groups are weaker acids than AlOH groups, lower pH would have favored bonding at the latter sites.

Ligand-exchange reactions of adsorbed copper

Exposure of moist samples to ammonia vapor following Cu^{2+} adsorption permitted the "availability" of adsorbed Cu for ligand exchange to be assessed (McBride, 1982), because the coordination of NH$_3$ to Cu^{2+} greatly shifts the ESR parameters. The interaction of sorbed Cu with NH$_3$ vapor on all allophanic samples, either undried gels, or air-dried samples that had been remoistened, is typified by sample SA 1.10 (Figure 10). The ESR parameters (Table 2) were independent of both SA ratio and sample preparation. The spectra were sufficiently complicated to prevent any meaningful estimation of parameters for the perpendicular spectral components.

The type and distribution of surface-bound species altered noticeably following their exposure to NH$_3$ when the samples were left uncovered at ambient temperature. Spectra observed at 22°C immediately after exposure to NH$_3$ (Figure 10A) indicate the existence of rigid-limit resonances at $g_\parallel$ = 2.225 and 2.266. The latter resonance was little influenced by time or temperature, being slightly shifted to 2.270 by freezing at −120°C and still present 24 hr after exposure to air (Figures 10B and 10C).

The resonance centered at $g_\parallel$ = 2.225 was sensitive to both time and temperature. With dehydration and loss of NH$_3$, this signal diminished as a new resonance at $g_\parallel$ = 2.311 appeared (Figure 10C). At high NH$_3$ concentrations (Figure 10A), freezing was associated with emergence of a new spectrum at $g_\parallel$ = 2.236–2.241 and loss of the $g_\parallel$ = 2.225 resonance (Figures 10B and 10C). This change was reversible on thawing. After much of the NH$_3$ had been lost by volatilization, however, the 2.311 resonance was unaffected by temperature change.

The rigid-limit Cu spectra of Figure 10 indicate the existence of motionally restricted copper-ammonia surface species. No evidence was noted for an isotropic spectrum; hence, intercalated or loosely bound Cu ions were absent. By comparison of these resonances with those of copper adsorbed on porous alumina and silica supports (Table 2), the rigid-limit spectrum at room temperature is tentatively assigned to Cu^{2+} equatorially coordinated to one surface Al–O group and 3 NH$_3$ ligands. Spectra with similar parameters have been reported for aluminum hydroxide surfaces that had been treated with Cu and NH$_3$ (Martini *et al.*, 1980; Mc-Bride, 1982; McBride *et al.*, 1984). Martini *et al.* (1980) attributed this spectrum to a bound cupric pentamine

Table 3. Copper and cobalt adsorbed on allophane ($SiO_2/Al_2O_3 = 1.34$) at specific pH and extractable by a single, 2-hr treatment.

Extractant	Cu extracted (mmole/kg) pH		Co extracted (mmol/kg) pH	
	4.90	6.20	6.60	7.90
0.01 M CaCl$_2$	1.8 (7)[1]	0.2 (<1)	2.1 (12)	0.7 (1)
0.05 M Pb(NO$_3$)$_2$	15.8 (59)	36.1 (55)	14.1 (80)	40.0 (67)
0.42 M CH$_3$COOH	25.0 (94)	61.2 (94)	15.6 (89)	54.7 (92)
0.05 M EDTA (pH 7)	22.3 (84)	59.5 (91)	13.9 (79)	49.4 (83)

[1] ( ) = % of total desorbed.

complex; i.e., they believed that the axial ligand positions were occupied by NH_3 rather than H_2O. Because of the tetragonal distortion of the ligand field of Cu^{2+}, these axial ligands are weakly held and have relatively small effects on the ESR parameters.

The second copper-ammonia complex observed at room temperature ($g_{\parallel} = 2.225$) was distinguished by its unusually low $g_{\parallel}$ value. Such a $g_{\parallel}$ value can result from association of adsorbed copper-ammonia complexes with silanol groups (Martini and Bassetti, 1979), but not with aluminol groups (Table 2). Thus, Cu^{2+} which was initially adsorbed at SiOH groups had its ligand water displaced by NH_3, as follows:

$$\diagdown\!SiO\text{--}Cu(H_2O)_4^+ + 4NH_3$$
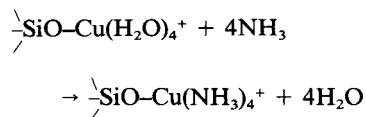
$$\rightarrow \diagdown\!SiO\text{--}Cu(NH_3)_4^+ + 4H_2O$$

In addition, the high pH generated by introduced NH_3 presumably favored Cu^{2+} bonding at silanol groups as they dissociated more fully. Assignment of the surface oxygen in $SiOCu(NH_3)_4^+$ to the weakly binding axial position of Cu^{2+} rather than an equatorial site is consistent with the observed lability of this species and the similarity of its $g_{\parallel}$ parameter with that of other tetragonal copper systems containing 4 nitrogen ligands in the equatorial plane (Martini and Burlamacchi, 1979).

As ammonia was allowed to volatilize and pH decreased, the $g_{\parallel} = 2.225$ resonance diminished, being replaced by that at $g_{\parallel} = 2.311$. A calculation of the distribution in solution of copper-hydroxy and copper-ammonia species as ammonia concentration varies up to 10 M for a fixed concentration of Cu^{2+}, reveals that only at high concentrations of NH_3 ($> 10^{-1}$ M NH_3 for 2.25×10^{-4} M Cu^{2+} (aq)) do soluble $Cu(NH_3)_4^{2+}$ and $Cu(NH_3)_5^{2+}$ cations predominate over $CuOH^+$ or $Cu(OH)_2^0$. Hence, as NH_3 is lost and pH decreases, hydrolysis of Cu-ammonia surface complexes can occur. Therefore, mixed copper-hydroxide-ammonia surface complexes, such as $AlO\text{--}Cu(OH)(NH_3)_2^0$, are possible, and may account for the 2.311 resonance that appeared with the partial escape of NH_3 from allophane.

Exposure of Cu-treated imogolite to NH_3 revealed the present of 3 species associated with imogolite at room temperature; a partially resolved, 4-line isotropic spectrum ($g_0 = 2.12$, $A_0 = 0.0082$ cm^{-1}) characteristic of copper-ammonia species tumbling freely in solution; and two ill-resolved, rigid-limit spectra, the more prominent at $g_{\parallel} = 2.266$ (possibly $Al\text{--}O\text{--}Cu(NH_3)_3^+$) and the weaker at $g_{\parallel} = 2.320$. The weaker retention of Cu^{2+} by imogolite in comparison to allophane as shown by this result and by the adsorption data (Figure 2) may be at least partly due to the fewer surface bonding sites relative to adsorbed Cu^{2+} for imogolite.

Lowering the temperature of NH_3-treated Cu-imogolite to $-120°C$ eliminated the isotropic and $g_{\parallel} = 2.320$ signals, and created a new resonance at $g_{\parallel} = 2.228$ (Table 2). The intensity of the isotropic signal at room temperature was correlated with the intensity of the rigid-limit 2.228 signal on freezing, the change between room and low temperature being completely reversible. The $g_{\parallel}$ value was sufficiently similar to that of Si–O–Cu $(NH_3)_4^+$ on allophane for the two species to be considered identical.

Imogolite consists of bundles of tubules 100–300 Å wide (Egashira, 1977), and under conditions of full hydration, intertubular pores are 11 Å in diameter (Wada and Henmi, 1972). At low temperature, tubes within a bundle can be expected to coalesce as a result of migration and freezing of intertubular water, leading to occluded concentration of NH_3 and $Cu\text{--}NH_3$ species considerably higher than in bulk solution. Under these circumstances, complex formation with exposed edge silanol groups on the interior of imogolite tubes may become more favorable as the equilibrium:

$$\diagdown\!SiOH + NH_3 + Cu(NH_3)_4(H_2O)_2^{2+}$$

$$\rightleftharpoons \diagdown\!Si\text{--}O\text{--}Cu(NH_3)_4^+ + NH_4^+ + 2H_2O$$
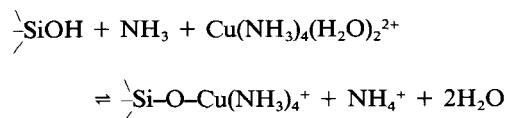
is forced towards the right. The reduced accessibility of silanols or greater degree of hydration of imogolite may have prevented this bond from forming readily at room temperature as it did with allophane.

Loss of the $g_{\parallel} = 2.320$ signal on imogolite at low temperature is readily understood, if by freezing, the

increased NH_3 concentration causes the following reversible ligand exchange:

$$NH_3(aq) +$$
$$Al-O-Cu(NH_3)_2OH \rightleftharpoons Al-O-Cu(NH_3)_3{}^+ + OH(aq)^-$$
$$(g_\parallel = 2.320) \quad (g_\parallel = 2.272)$$
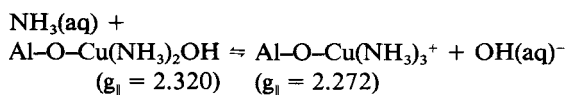
Extractability of sorbed species

Extractability of the sorbed trace metals was ascertained using the synthetic SA 1.34 allophane sample adjusted to two different pHs in order to vary the adsorption level. The extractants partitioned the absorbed metal into several categories; water soluble and cation exchangeable (0.01 M $CaCl_2$), exchangeable by Pb^{2+} or H^+, and surface species labile enough to be chelated by EDTA.

Water-soluble and cation-exchangeable Cu and Co were expectedly low (Table 3) because Ca^{2+} generally shows little affinity for oxide surfaces at neutral pH other than in trace amounts (Kinniburgh *et al.,* 1975). Pb, however, was able to exchange an appreciable fraction of the sorbed species (Table 3), a consequence of the high affinity of Pb^{2+} (comparable to that of Cu^{2+}) for hydrous oxides (Kinniburgh and Jackson, 1981). The release of large quantities of sorbed metal into solution by EDTA and CH_3COOH indicates that the metal-oxide bonds could have been broken by competition with a chelating agent or by proton attack.

An ESR spectrum was obtained for each of the samples from which considerable amounts of Cu had been extracted to determine whether removal from either of the two sites proposed above was preferred. In each sample, the residual Cu spectrum contained a high-field $g_\perp$ absorbance that had increased relative to its low-field companion, implying that the surface Cu species presumably bonded to AlOH groups by a binuclear linkage resisted dissolution by the extracting agents.

SUMMARY

Cu and Co were specifically adsorbed on both allophane and imogolite. The selective preference of Cu over Co, increased adsorption as pH was raised over a narrow range, concomitant release of protons, and removal of ions from solution undersaturated with respect to the least soluble hydroxide or hydroxycarbonate phase are characteristics associated with a specific adsorption mechanism (Barrow *et al.,* 1981). The adsorption of Cu on allophane was dependent on the SiO_2/Al_2O_3 ratio of the synthetic adsorbent and increased with increasing alumina content. For adsorption on soil clays, however, the effect of SiO_2/Al_2O_3 ratio was unpredictable. With Co adsorption, which occurred at higher pH, no consistent effect of SiO_2/Al_2O_3 ratio was detected.

The ESR spectra suggest that monomeric Cu^{2+} adsorbed on an alumina-like surface at sites where surface hydroxyl was coordinated to a single Al ion, possibly by the displacement of two protons to form a binuclear complex with surface oxyanions on adjacent structural aluminum ions. In addition, bonding occurred at a second site, with the distribution of Cu between these two surface sites being dependent on the SiO_2/Al_2O_3 ratio, pH, and adsorbate concentration. The second site was likely a single SiOH or AlOH group, that bonded Cu^{2+} less energetically with the displacement of a single proton from the surface.

The exposure of surface-bound Cu^{2+} on allophane and imogolite to NH_3 resulted in an exchange of H_2O and/or OH^- ligands to generate Cu^{2+}-ammonia-surface complexes. For imogolite, some Cu^{2+} was desorbed from the surface as $Cu(NH_3)_4{}^{2+}$ ions. Dissolution of sorbed Cu and Co was readily achieved by complexation with EDTA and by other cations (Pb^{2+} or H^+) capable of displacing the metal by competing for its surface site.

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Резюме—Адсорбция Cu^{2+} и Co^{2+} на синтетическом имоголите и синтетических аллофанах в диапазоне различных отношений SiO_2/Al_2O_3, и на аллофановых глиновых фракциях из вулканическо-золовых почв измерялась в ионовой среде 0,05 М раствора $Ca(NO_3)_2$. Эффекты величины pH (и концентрации металла) на значение адсорбции были качественно похожи для обоих, синтетических аллофанов и природных глин, с небольшой разницей в поведении, вызванной разными отношениями SiO_2/Al_2O_3. Cu и Co хемосорбировались на аллофанах при pH = 5,0–5,5 и pH = 6,9–7,2 (величины pH для 50% уровня адсорбции) соответственно, с сопутствующим выделением 1,6–1,9 протонов на ион адсорбированного металла. Количественно, адсорбция на имоголите была меньше, чем на аллофанах, вероятно потому, что меньше мест доступных хемосорбции находится на трубчатой структуре имоголита. Исследования при помощи электронного спинового резонанса (ЭСР) показали, что Cu^{2+} адсорбировался в виде мономера на двух типах поверхностных мест. Предпочтительными местами являлись, вероятно, группы AlOH, связывающие Cu^{2+} путем бинуклеарного механизма; более слабые связи находились на одиночных группах AlOH или SiOH. Эти хемосорбированные типы Cu^{2+} выделялись быстро при помощи ЭДТА, CH_3COOH и металлов, способных к специфической адсорбции, но они не заменялись. Добавочно, лиганды H_2O или OH^- хемосорбированных Cu^{2+} заменялись быстро с NH_3, формируя комплексы, состоящие из трех составных частей Cu-аммиак-поверхность. [E.G.]

Resümee—Die Adsorption von Cu^{2+} und Co^{2+} durch synthetischen Imogolit und synthetische Allophane mit verschiedenen SiO_2/Al_2O_3-Verhältnissen sowie durch Allophan-haltige Tonfraktionen aus vulkanischen Aschenböden wurde in einem ionischen Medium von 0,05 m $Ca(NO_3)_2$ gemessen. Die Auswirkungen des pH-Wertes (und der Metallionenkonzentration) auf die Adsorption war für die synthetischen Allophane und natürlichen Tone qualitativ ähnlich, wobei die verschiedenen SiO_2/Al_2O_3-Verhältnisse nur relativ geringe Veränderungen hervorrufen. Cu und Co wurden durch Allophan bei pH 5,0–5,5 bzw. 6,9–7,2 (pH-Werte bei 50-prozentiger Adsorption) chemisorbiert, wobei gleichzeitig 1,6–1,9 Protonen pro adsorbiertem Metallion freigesetzt wurden. Quantitativ gesehen war die Adsorption durch Imogolit geringer als die durch die Allophane, wahrscheinlich wegen der geringeren Anzahl von Plätzen, die für die Chemisorption auf der röhrenförmigen Struktur von Imogolit zur Verfügung stehen. Elektronenspinresonanz-Untersuchungen (ESR) von Imogolit und den Allophanen zeigten, daß Cu^{2+} als ein Monomer an zwei Arten von Oberflächenplätzen adsorbiert wird. Die bevorzugten Plätze sind wahrscheinlich AlOH-Gruppen, die das Cu^{2+} durch einen binuklearen Mechanismus binden; eine schwächere Bindung erfolgt an einzelne AlOH- oder SiOH-Gruppen. Das auf diese Arten chemisorbierte Cu^{2+} wurde durch EDTA, CH_3COOH und Metalle, die eine spezielle Adsorption aufweisen, sehr leicht extrahiert, aber sie waren nicht austauschbar. Außerdem wurden die H_2O- und/oder OH^--Liganden des chemisorbierten Cu^{2+} sehr leicht durch NH_3 ersetzt, wobei ternere Cu-Ammoniak-Oberflächenkomplexe gebildet werden. [U.W.]

Résumé—L'adsorption de Cu^{2+} et Co^{2+} per l'imogolite synthétique, par des allophanes synthétiques avec une gamme de proportions SiO_2/Al_2O_3, et par des fractions d'argile allophanique de sols volcaniques a été mesurée dans un milieu ionique de 0,05 M $Ca(NO_3)_2$. Les effets du pH (et la concentration du métal) sur l'adsorption étaient qualitativement semblables pour les allophanes synthétiques et les argiles naturels, avec des changements de comportement relativement mineurs causés par des proportions SiO_2/Al_2O_3 variables. Cu et Co étaient chemisorbés par l'allophane aux pH 5,0–5,5 et 6,9–7,2 respectivement (valeurs de pH pour le niveau d'adsorption de 50%), avec relâchement concordant de 1,6–1,9 protons/ion métal adsorbés. Quantitativement, l'adsorption par l'imogolite était moindre que par les allophanes, probablement parce qu'il y a moins de sites disponibles pour la chémisorption sur la structure tubulaire de l'imogolite. Les études de spin à résonance d'électrons (ESR) de l'imogolite et des allophanes ont révélé que Cu^{2+} était adsorbé comme monomère sur deux types de sites de surface. Les sites préférés étaient des groupes AlOH probables liant Cu^{2+} par un mécanisme binucléaire, on trouve des liens plus faibles sur les groupes AlOH ou SiOH simples. Ces formes de Cu^{2+} chémisorbées étaient facilement extraites par EDTA, CH_3COOH, et par des métaux capables d'adsorption spécifique, mais n'étaient pas échangeables. De plus, les ligands de H_2O et/ou de OH^- de Cu^{2+} chémisorbé étaient facilement déplacés par NH_3 avec la formation de complexes de surface Cu-ammonium ternaire. [D.J.]