

CATION AND ANION RETENTION BY NATURAL AND SYNTHETIC ALLOPHANE AND IMOGOLITE

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Abstract—The negative surface charge of synthetic allophanes with a range of Si/Al ratios decreased and positive charge increased with increasing alumina content at a given pH. The phosphate adsorption capacity also increased with increasing Al content. That this relationship between composition and chemical reactivity was not found for the soil allophanes is attributed to the presence of specifically adsorbed organic or inorganic anions on the natural material. Both synthetic and natural imogolites had a much lower capacity to adsorb phosphate than the allophanes and adsorbed anomalously high amounts of Cl^- and ClO_4^- at high pH. It is proposed that intercalation of salt occurs in imogolite, although electron spin resonance studies using spin probes failed to reveal the trapping of small organic molecules in imogolite tubes. These spin probes in the carboxylated form did, however, suggest an electrostatic retention of carboxylate by imogolite and a more specific adsorption by allophane involving ligand exchange of surface hydroxyl. The results illustrate the inherent differences in charge and surface properties of allophane and imogolite despite the common structural unit which the two minerals incorporate.

Key Words—Adsorption, Allophane, Anion retention, Cation retention, Imogolite, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, Surface charge.

INTRODUCTION

Allophane and imogolite are both important constituents in soils of volcanic origin. Imogolite has a tubular structure, $\sim 20\text{--}22$ Å in diameter, caused by curling of a gibbsite sheet on replacement of an hydroxyl layer by orthosilicate anions. The overall composition can be represented by the idealized formula $\text{HOSiO}_3\text{Al}_2(\text{OH})_3$ (Cradwick *et al.*, 1972). The structure of allophane, however, is open to interpretation, although it possesses several undisputed physical and chemical features. Allophane consists of discrete hollow spherules, or polyhedra, $35\text{--}50$ Å in diameter (Henmi and Wada, 1976) with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios between 1 and 2. The “proto-imogolite” allophane form (Al/Si = 2) is constructed of imogolite structural units (Farmer *et al.*, 1979; Parfitt and Henmi, 1980). Other forms of allophane may exist in nature such as the feldspathoid-like material that can be synthesized under alkaline or slightly acid conditions (Farmer *et al.*, 1979).

The synthetic method of Wada *et al.* (1979) has demonstrated that allophanes can be produced hydrothermally using realistically low concentrations of silicic acid monomer and hydroxy-aluminum ion. The gels are morphologically similar to their natural counterparts. By using restricted ratios of silicic acid and hydroxy-aluminum at acid pH, imogolite can be similarly prepared (Farmer and Fraser, 1978).

The sign and magnitude of surface charge of these amphoteric materials is dependent on a number of

factors: pH, cation type and concentration of electrolyte, the silica content of the hydrous aluminosilicate phase, presence of organic matter, and the specific adsorption of ions like phosphate or sulfate (Gillman, 1981; Gonzales-Batista *et al.*, 1982; Perrott, 1977, 1978a; Rajan, 1979; Wada, 1980; Wada and Ataka, 1958; Wada and Harada, 1969). The tubular morphology of imogolite may exert an influence on surface charge measurement that is contrary to predictions based on allophane, because experiments with natural and synthetic imogolites have revealed that substantial positive charge remained at neutral-alkaline pH (Theng *et al.*, 1982). Allophane has essentially zero positive charge in this pH range. Consideration of the imogolite structure precludes the possibility of permanent positive charge; hence, explanations of positive charge must be related either to the porous structure and properties of interstitial solution or to specific adsorption, as hypothesized by Theng *et al.* (1982).

The dependence of imogolite surface charge on the anionic species (perchlorate, chloride, and carboxylate spin probes) is described here, and a comparison is made of surface charge and phosphate adsorption on natural and synthetic allophane and imogolite.

MATERIALS AND METHODS

Samples

The clay fractions from three field-moist volcanic ash soils of New Zealand and Japan, whose mineralogies and chemical properties have previously been characterized, were selected on the basis of their $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and high allophane contents. The Egmont sample (Eg) contains “proto-imogolite” allophane and

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is comparable with Parfitt and Henmi's (1980) sample 923. The properties of the Te Akatea (Te Ak) and Kakino (KnP) allophanes were reported by Perrott (1977) and Henmi *et al.* (1981), respectively. The clays ($<2\ \mu\text{m}$) were isolated by centrifugation after overnight mechanical dispersion in distilled water, and used without further chemical pretreatment. Imogolite gel (KiG) separated from the Kitakami pumice bed (Wada and Matsubara, 1968) was pretreated with peroxide, citrate-bicarbonate-dithionite, and 2% Na_2CO_3 before ultrasonic dispersion at pH 4.

Allophanic gels (Wada *et al.*, 1979) were prepared in 11-liter batches. In each batch, aliquots of freshly prepared and standardized aluminum chloride were added to 0.002 M monomeric silicic acid solution, obtained by hydrolysis of an ethanolic solution of tetraethyl silicate, with the subsequent addition of 0.1 M NaOH to give an OH/Al molar ratio of 3. Products isolated from parent solutions with Si/Al ratios of 1.25, 2, or 5 are labelled according to their solid silica/alumina ratio (Table 1).

Synthetic imogolite (Farmer *et al.*, 1977a; Farmer and Fraser, 1978) was similarly prepared in large volumes. Hydrolyzed tetraethyl silicate (0.004 M) and aluminum perchlorate (0.0072 M) were partially neutralized to pH 5 with 1 M NaOH. This solution was immediately acidified with an acetic acid (0.44 M)–perchloric acid (0.6 M) solution and heated to 95°C under reflux conditions for 5 days.

Both natural and synthetic samples were flocculated by the addition of NaCl; the excess salt was removed by dialysis. The solid materials were isolated by drying the suspensions in a solvent evaporator. All results are expressed on a 150°C oven-dry clay basis (Parfitt and Henmi, 1980). Characterization was by differential thermal analysis (DTA), transmission electron microscopy (TEM), electron diffraction, and infrared absorption spectroscopy (IR).

Chemical analysis and phosphate adsorption

Silicon and aluminum were determined colorimetrically on acidified sodium-fusion extracts containing 50 mg of synthetic samples, aluminum using the hydroxyquinoline-butyl acetate technique of Bloom *et al.* (1978), and silicon by the molybdenum blue method of Weaver *et al.* (1968). Suspensions containing 20 mg of the clays were shaken in the dark with 25 ml of 0.15 M sodium oxalate (pH 3.5) at 22°C for 2 hr in order to dissolve allophane, imogolite, and poorly ordered hydrous metal oxides selectively (Higashi and Ikeda, 1974). Oxalate was destroyed by $\text{HNO}_3/\text{H}_2\text{SO}_4$ digestion prior to Al and Fe measurement by colorimetry in hydroxyquinoline-butyl acetate at 395 and 600 nm, respectively. Total dissolved silicon was determined as above, but only after aliquots of oxalate digest had been fused in sodium hydroxide and acidified.

Phosphate adsorption was conducted by the procedure of Parfitt and Henmi (1980) and measured by the standard phosphomolybdate colorimetric method.

Electron spin resonance and surface-charge measurements

Suspensions containing 200 mg sample and 10 ml of electrolyte were equilibrated for 16 hr with 0.01 M NaCl, 0.1 M NaCl, or 0.01 M NaClO_4 . Suspension pH was adjusted to predetermined levels by the frequent additions of small aliquots of 0.1 M NaOH, HCl, or HClO_4 . Sodium and chloride were determined in solution after centrifuge-washing suspensions with 0.05 M $\text{Ca}(\text{NO}_3)_2$, sodium by flame emission, and chloride with mercury(II) thiocyanate (Florence and Farrar, 1971). When sodium perchlorate was the electrolyte, the washing solution was altered to 0.05 M CaCl_2 and perchlorate was determined potentiometrically with an Orion nitrate electrode.

Nitroxide spin probes, the anionic 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (TEMPO-COOH) and uncharged 2,2,6,6-tetramethyl-4-piperidinone-1-oxyl (TEMPONE) were used to study surface-charge development by electron spin resonance (ESR). Aqueous suspensions containing 50 mg of a synthetic sample in 10 ml of probe (10^{-4} M) were equilibrated for 30 hr. Periodic adjustments were made with 0.1 M NaOH and 0.1 M HClO_4 to establish a pH range between 4 and 10. The amount of adsorbed TEMPO-COOH probe was determined by sampling centrifuged supernatants with a capillary and taking ESR spectra on a Varian E-104 (x-band) spectrometer. Probe adsorption was determined by using the decrease in signal intensity of the central peak in the isotropic solution spectrum. Wet minerals, washed free of nonadsorbed probe, were also sampled in capillary tubes for ESR analysis.

RESULTS AND DISCUSSION

Structural properties of materials

The purity of the natural and synthetic samples was ascertained by electron diffraction, differential thermal, infrared, and transmission electron microscopic analyses. The Egmont and Kakino clay fractions contained about 7% and 15%, respectively, by weight oxalate-insoluble impurities (mostly glass) and insignificant quantities of imogolite. The Te Akatea clay was completely solubilized by acid oxalate.

The infrared (IR) patterns of the synthetic allophanes were similar to those reported for allophanes (Wada *et al.*, 1979). The Si–O stretching absorption (Figure 1) shifted to higher frequencies, from 970 to 1000 cm^{-1} , as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio increased, and other absorption peaks indicative of allophane were recorded near 570, 428, and 348 cm^{-1} . Very diffuse electron diffraction patterns gave d-spacings close to 1.3, 2.1, and 3.5 Å. Diagnostic IR bands assigned to the tubular mor-

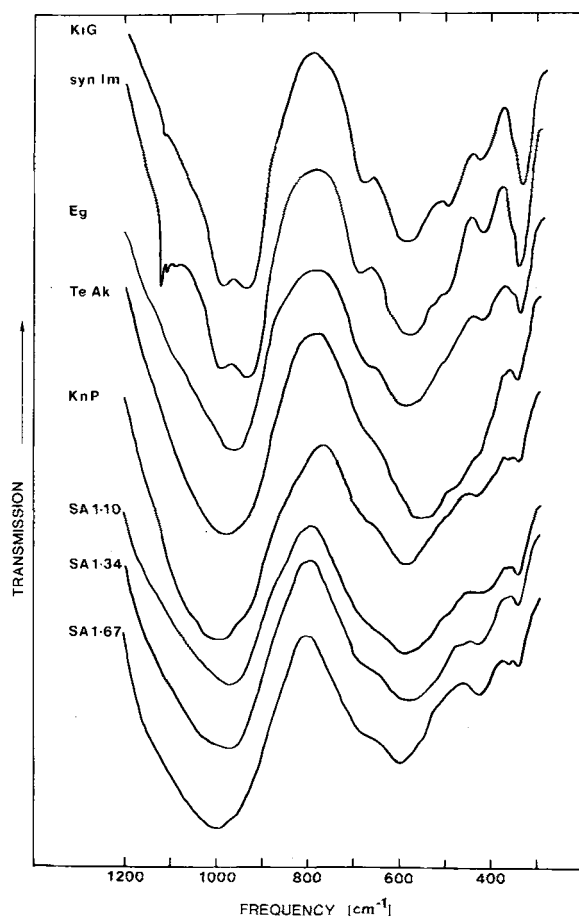


Figure 1. Infrared spectra of samples heated to 150°C in KBr discs.

phology of "imogolite" structures at 995 and 348 cm^{-1} were clearly evident (Figure 1). Peaks at 1120 cm^{-1} , due to adsorbed ClO_4^- retained by the structure, persisted despite prolonged dialysis. Electron diffraction patterns of parallel alignments of synthetic imogolite tubes gave d-spacing at 15.5, 9.2, 6.68, 5.25, 4.2, 3.27, 2.3, 2.1, and 1.4 Å, indicating the expected presence of 8.4-Å repeat units along the tube axis and center-to-center tube separations of 27 Å.

Chemical properties

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios for the synthetic samples and the oxalate-soluble fraction of the natural clay samples (Table 1) reveal the expected values for allophane (1-2) and imogolite (1.0). Using the intensity of the 348- cm^{-1} IR band (Farmer *et al.*, 1977b), the proportion of "proto-imogolite" allophane in samples Eg, Te Ak, and KnP was estimated to be 64, 34, and 27% respectively; the last value is from Parfitt *et al.* (1980). Of a preliminary series of synthetic gels examined, one sample with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.03$ contained 64% imogolite structures, the level decreasing as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio increased. Evidently, pure "proto-imogolite" allophane does not form under the pH conditions (6-6.5) employed to synthesize allophane with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.0$. Admixtures of several "allophanic" materials may form at these relatively high pHs.

Phosphate adsorption

Phosphate adsorption isotherms are shown in Figures 2 and 3. The molar quantity of adsorbed phosphate in equilibrium with a solution concentration of 10^{-6} M PO_4 was used to measure "reactive AlOH ," sites at which phosphate is specifically adsorbed on adjacent structural aluminum ions (Parfitt and Henmi, 1980). Reactive AlOH , as shown in Table 1, decreased

Table 1. Chemical characterization of allophane and imogolite samples.

Sample	Composition (wt. %)					$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio	AlOH^4 (mole/kg)
	C ¹	Si ²	Al ²	Fe ²	H_2O^{+3}		
Egmont soil clay, New Zealand	5.8	8.7	17.6	3.3	26	0.95	0.16
Te Akatea soil clay, New Zealand	0.6	15.4	19.6	2.9	15	1.51	0.32
KnP soil clay, New Zealand	0.1	11.1	14.9	4.4	13	1.43	0.07
Synthetic allophane	—	13.9	24.2	—	16	1.10	0.22
Synthetic allophane	—	16.1	23.0	—	15	1.34	0.15
Synthetic allophane	—	17.7	20.4	—	15	1.67	0.10
KiG (imogolite gel) ⁶	—	13.1	23.5	—	18	1.07	0.003
Synthetic imogolite	—	12.6	23.1	—	23	1.05	0.10
Imogolite ⁵	—	14.1	27.2	—	18.2	1.00	—

¹ Easily oxidizable carbon.

² Determined on sodium hydroxide fusions of acid oxalate extracts for natural samples and sodium hydroxide fusions of synthetics.

³ Weight loss between 150°C and 650°C after 4 hr heating.

⁴ "Reactive aluminum hydroxide" by phosphate adsorption.

⁵ Ideal structure.

⁶ Separated from Kitakama pumice bed (Wada and Matsubara, 1968).

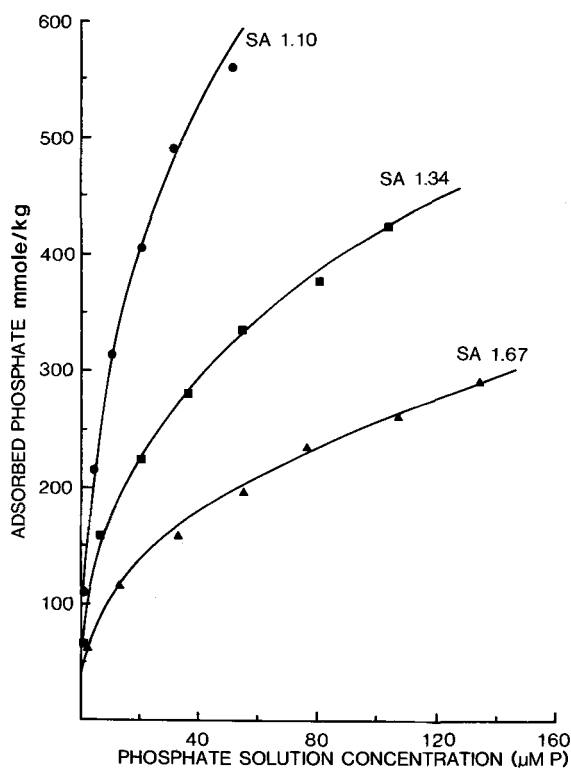


Figure 2. Phosphate adsorption isotherms of synthetic allophanes in 0.01 M CaCl_2 . SA = $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the allophanes.

with decreasing alumina content in the synthetic allophanes not only as a consequence of the reduced number of AlOH groups, but probably also as a result of the blocking of sites by mono- or polymeric silicate species. The affinity of synthetic allophanes for PO_4 was related to the alumina content (Figure 2); however, the same trend was not observed for the soil allophanes (Figure 3). These results may depend on factors inherited from the soil environment, such as the prior absorption of fulvic acids and other specifically adsorbed anions (Perrott, 1978b). The low PO_4 adsorption capacity and reactive AlOH of sample Eg, the most aluminous sample examined, may therefore be explained by the high organic content of this clay (Table 1).

Peripheral $\text{Al}(\text{OH})\text{H}_2\text{O}$ groups located at either extremity of the imogolite tube are likely sites for reaction with phosphate. Assuming that each tube of natural imogolite can be represented by an annulus containing 11 unit cells, with an average length of $1.5 \mu\text{m}$ (Wada, 1980), the calculated amount of reactive AlOH is 3.0×10^{-3} mole/kg, in excellent agreement with the result for sample KiG determined from phosphate adsorption (Table 1). For the synthetic imogolite tubes, corresponding annulus parameters are taken as 14 unit cells with an average length of 600 \AA . The length mea-

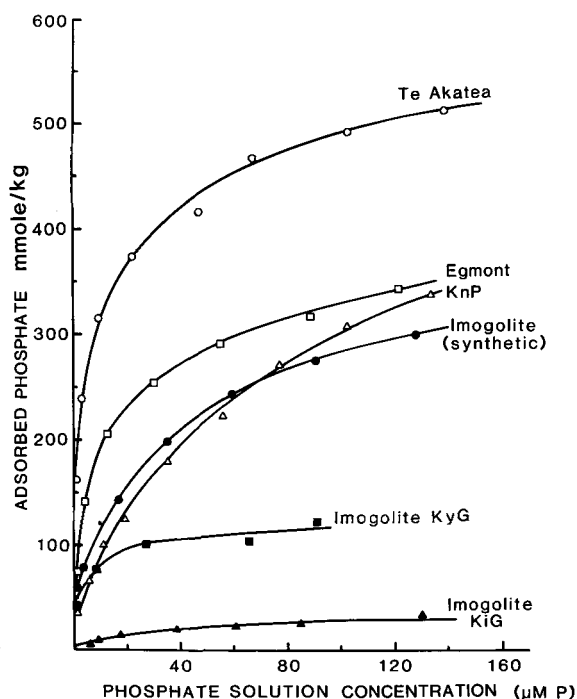


Figure 3. Phosphate adsorption isotherms of allophanic clay, imogolite, and synthetic imogolite samples in 0.01 M CaCl_2 . Data for sample KyG imogolite taken from Theng *et al.* (1982).

surement is somewhat subjective because electron micrographs show the tubular development in synthetic preparations to be quite haphazard. Calculation based on these dimensions leads to 70×10^{-3} mole/kg of reactive AlOH , approximately equal to the measured value for the synthetic preparation.

Surface charge

Positive and negative surface charge as measured by adsorption of sodium and chloride in 0.1 M NaCl suspensions were pH-dependent (Figures 4–6). Charge development (Figure 4) was also related to the alumina content, negative charge decreasing and positive charge increasing at a given pH with increasing alumina. The zero point of charge (ZPC) values were 6.9, 6.5, and 5.5 for the synthetic analogues with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 1.10, 1.34, and 1.67, respectively, with corresponding values of 6.2 for samples Te Ak and Eg, and 5.0 for sample KnP. Similar observations were noted by others for allophanic soils and synthetic allophanes (Gonzales-Batista *et al.*, 1982; Perrott, 1977).

Negative and positive charge development (Figures 4 and 5) was qualitatively similar to the combined charge properties of pure hydrous silica and alumina. In general, the allophanes had a smaller positive charge than the alumina and a larger negative charge than the silica at a given pH. The association between alumina

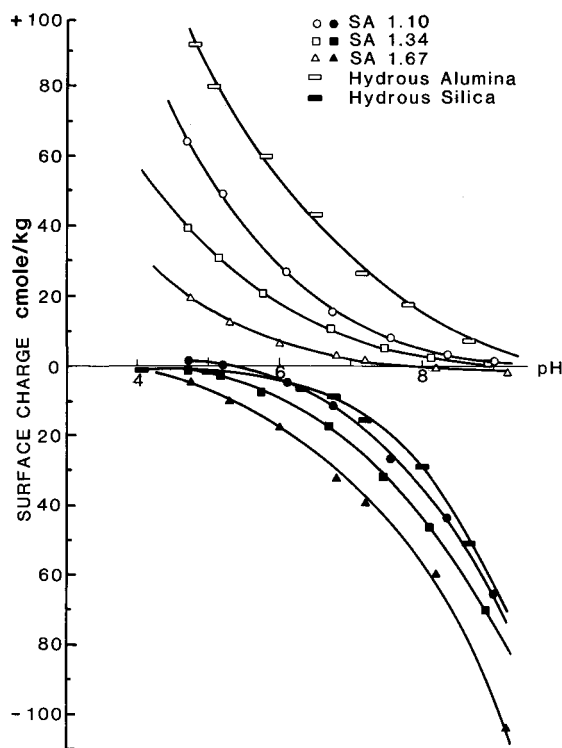


Figure 4. Surface charge of synthetic allophanes, hydrous alumina, and hydrous silica, measured by Na^+ (closed symbols) and Cl^- (open symbols) adsorption from 0.1 M NaCl as a function of pH. SA = $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios.

and silica in allophane may generate more acidic Al-OH or Si-OH groups, although the very high specific surface area of allophane could account for the larger negative charge compared with silica.

Relative to allophane, the surface charge of imogolite was anomalous. The data in Figures 2–6 show that the allophanes readily adsorbed Cl^- and phosphate at low pH in comparable quantities, whereas the imogolites (especially sample KiG) adsorbed more Cl^- than phosphate. High residual positive charge at $\text{pH} > 8$ was not evident for allophane or alumina (Figure 4), with little change if the electrolyte was changed from NaCl to NaClO_4 . In contrast, positive charge on imogolite appeared to be anion dependent, based on the fact that 0.01 M NaCl and NaClO_4 media generated somewhat different positive charges but identical negative charges (Figure 6).

Accurate charge measurement depends on how precisely the amount of nonadsorbed salt in entrained solution of the gel can be estimated. Mass loss at 105°C was taken as a measure of occluded solution, and corrections were made assuming that the mass loss represented the quantity of occluded solution having the same ion concentration as the bathing electrolyte. Adjunct requirements are that dehydration of occluded

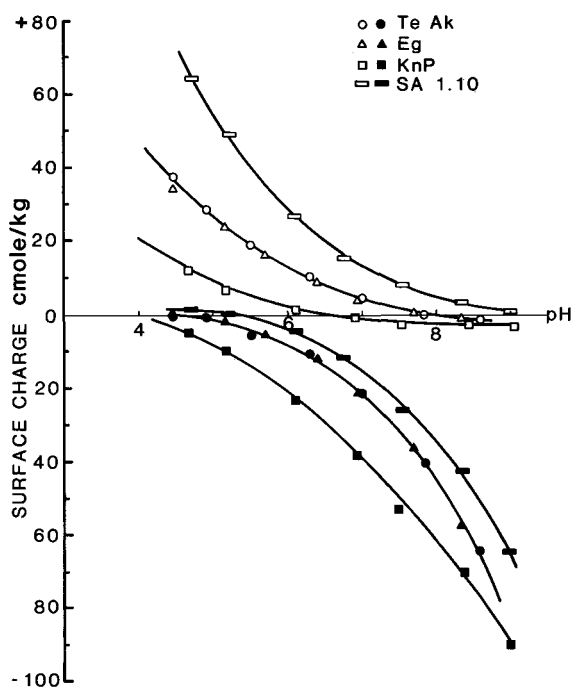


Figure 5. Surface charge of allophanic clays measured by Na^+ (closed symbols) and Cl^- (open symbols) adsorption from 0.1 M NaCl as a function of pH. SA = $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

solution was complete at 105°C , and that neither specific adsorption nor intercalation of salt occurred. The charge behavior of imogolite appeared to be anomalous because of a failure of one or more of these assumptions to apply.

ESR spin probes were used to determine whether or not the adsorption of Cl^- at high pH was due to coulombic attraction. No evidence of adsorbed probe anion (TEMPO-COO^-) was found in washed, centrifuged imogolite suspensions above $\text{pH} 9.5$. In fact, adsorption of the organic anion (Figure 7) followed a trend between $\text{pH} 5$ and 10 expected for materials with pH-dependent positive surface charge. To verify that the ESR signals at any pH were not the result of physical trapping, the presence of TEMPONE, an uncharged nitroxide probe, was monitored in suspension after the introduction of ascorbic acid, an effective reducing agent for nitroxides. All of the probe was reduced immediately, suggesting no entrapment of probe molecules in imogolite. Thus, the diffusion of probes into inter- and intratubular pores was not evident, possibly because the probe molecules are somewhat too large ($7\text{--}8 \text{ \AA}$ diameter) to enter the tube holes. Because the probe experiments revealed that $\text{pH} 9.5$ is the highest pH at which any surface positive charge can be expected, the observation of adsorbed Cl^- near this pH (Figure 6) suggests an artifact in the method or implies the existence of a mechanism of Cl^- retention that does not

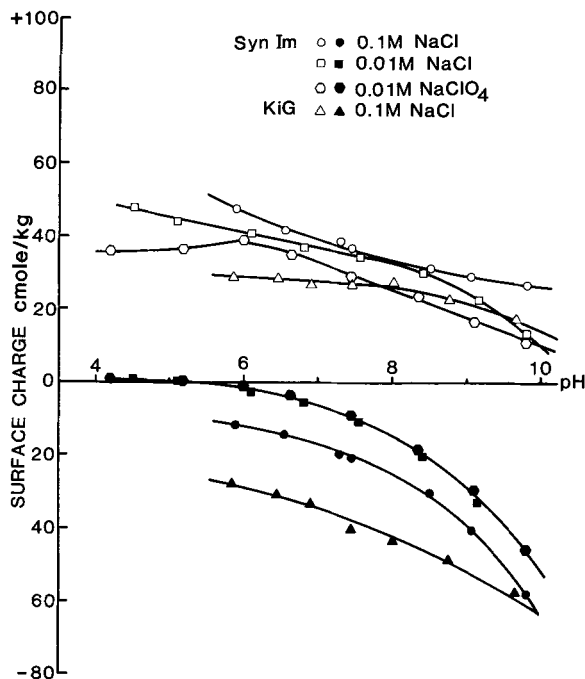


Figure 6. Surface charge of imogolite measured by Na^+ (closed symbols) and Cl^- or ClO_4^- (open symbols) adsorption as a function of pH.

apply to the organic probe anion. Whereas intercalation of salt in the inter- or intratubular pores seems a reasonable explanation of the anomalous behavior of imogolite, the phenomenon must be pH-dependent inasmuch as the imogolites retained no Na^+ ions from 0.01 M NaCl or NaClO_4 at pHs < 6 (Figure 6). Salt intercalation requires that equimolar quantities of Na^+ and anion be adsorbed.

Penetration of anions into the intratubular volume may be possible despite the obstacle to diffusion presented by a tube with a very small internal diameter. Using a one-dimensional random-walk model (Atkins, 1982), calculations show that diffusion into tubes 1 μm in length is quite rapid if steric hindrance to molecular motion is neglected. At low pH, however, Na^+ adsorption on the synthetic imogolite was negligible (Figure 6), suggesting that any intercalation that did occur must have utilized H^+ ions to balance the anion charge.

Considering that the natural imogolite (sample KiG) had the most highly developed tube structure, intratubular intercalation should have been most evident for this sample. The data indicate more retention of anions at high pH and more retention of cations at low pH than expected when compared with the results for allophane (Figure 6). The natural imogolite retained more Na^+ than the synthetic imogolite at low pH, again suggesting an adsorption process enhanced by a tubular morphology.

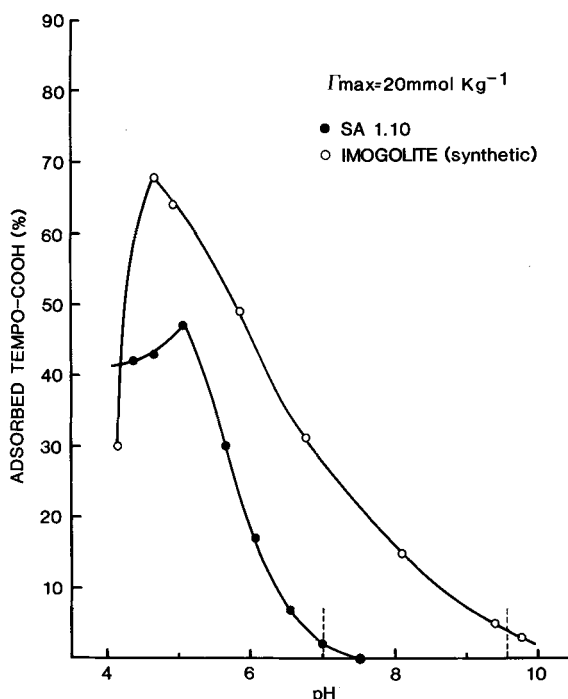


Figure 7. Adsorption of spin probe (10^{-4} M TEMPO-COOH) by synthetic allophane and imogolite as a function of pH. The dashed vertical lines indicate the pH above which no positive charge was detected by probe retention in washed suspensions. SA = $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

Adsorption of ESR spin probes

To adsorb TEMPO-COOH over a range of pH it was necessary to adjust the suspension pH using small aliquots of 0.1 M NaOH and 0.1 M HClO₄. The introduction of anions, ClO_4^- and OH^- , provided species capable of competing with the carboxylate probe to balance surface charge. Introduced perchlorate, greatly exceeding the probe concentration, was responsible for the decreased adsorption of probe in allophanic and imogolitic suspensions at pH < 5.05 (Figure 7), coupled with decreased dissociation of the carboxylate group at acidic pH values.

ESR spectra of suspension samples washed free of excess probe were obtained using the samples from the probe-adsorption experiments. Irrespective of pH, imogolite suspensions gave characteristic three-line isotropic spectra, very similar to the spectrum of probe in free solution (Figure 8A). The rotational correlation time (τ_c) was determined as described elsewhere (McBride, 1980). Using the parameters from the spectrum in Figure 8A, τ_c was estimated at 4.6×10^{-11} sec, typical of small nitroxide probes tumbling in solution. The probe's mobility in imogolite, $\tau_c = 1.5 \times 10^{-10}$ sec, was reduced relative to free solution; however, its motional behavior remained "solution-like" and unaf-

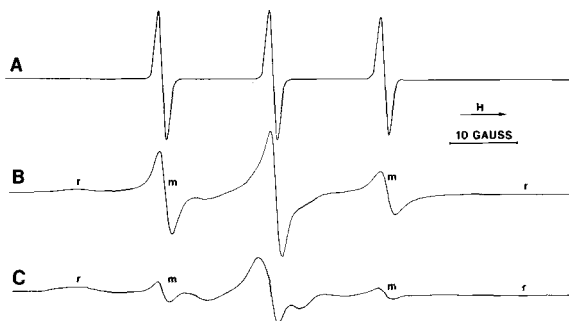


Figure 8. Room temperature electron spin resonance spectra of aqueous 10^{-4} M TEMPO-COOH: A = with no adsorbent present; B = after 30-hr reaction with allophane ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.10$) and removal of excess probe at pH 4.35; C = after a 20-min equilibration of the suspension described in B with 1 M NaCl. The letters "m" and "r" mark the outer resonance peaks of the mobile and rigid fractions of adsorbed TEMPO-COOH, respectively.

ected by pH. No probe was retained above pH 9.5, a pH at which no protonated Al-OH_2^+ surface groups should remain. The exchangeable nature of this mobile probe was verified by washing with 1 M ClO_4^- which removed all the probe from suspension.

The adsorption maximum of allophane (Figure 7) was less affected by anionic competition than that of imogolite, possibly because adsorption occurred by two mechanisms. One form of adsorbed TEMPO-COOH was relatively mobile ($\tau_c \approx 10^{-9}$ sec); the outer limits of this spectrum are labelled by "m" in Figures 8B and 8C. The second form was identified by high- and low-field resonances arising from rigid or near-rigid probe molecules ($\tau_c > 10^{-8}$ sec), labelled "r" in Figures 8B and 8C. These rigid limit spectra were observed in the pH range 4.35–5.05, with maximum intensity at pH 4.35. Treatments with 1 M ClO_4^- and 1 M Cl^- selectively desorbed the more mobile fraction, but were unable to exchange all the adsorbed probe (Figure 8C), a behavior unlike that of imogolite.

The results indicate the presence of two types of adsorbed probe in aqueous suspension: a loosely bound probe, possibly held electrostatically by AlOH_2^+ and readily exchanged by nonspecifically adsorbed anions like ClO_4^- , and a rigidly bound probe, probably arising from ligand exchange of surface hydroxyl. The second type, while not observed on imogolite, is evident on allophane and noncrystalline alumina (McBride, 1982).

CONCLUSIONS

Despite their common structural units, allophane and imogolite reveal inherent differences in charge and surface properties. The salt retention technique alone is inadequate to measure charge development on imogolite because it is impossible to separate the contributions from specific adsorption, intercalation, and

electrostatic attraction. When the adsorbing anion is large, possibly too large to penetrate the intratubular holes (e.g., TEMPO-COO^-), pH-dependent positive charge qualitatively follows the expected pattern as typified by hydrous alumina. However, the smaller inorganic anions (Cl^- , ClO_4^-) appear to be retained in imogolite gels at high pH in quantities inconsistent with expected charge properties of noncrystalline aluminosilicates, suggesting intercalation within the imogolite tubes.

For anions with large binding constants like phosphate, adsorption on allophane and imogolite is related to the number of defect "edge" sites, and phosphate adsorption on allophane exceeds that on imogolite particularly when the tubular structure of imogolite is well developed. Phosphate adsorption and surface charge depend on the alumina content of allophanic clays as has been described in other studies (Fey and Le Roux, 1976; Perrott, 1977; Gonzales-Batista *et al.*, 1982).

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Резюме—При данным pH и увеличивающимся содержании окиси алюминия отрицательный поверхностный заряд синтетических аллофанов с различными отношениями Si/Al уменьшался, а положительный заряд—увеличивался. Способность адсорбции фосфата также увеличивалась. Факт, что эта зависимость между составом и химической активностью не находилась для почвенных аллофанов, объясняется присутствием специфически адсорбированных органических и неорганических анионов в натуральном материале. Оба, синтетический и натуральный, имоголиты имели значительно меньшие способности адсорбции фосфата, чем аллофаны, и адсорбировали аномально большие количества Cl^- и ClO_4^- при больших величинах pH. Предполагается, что прослойка соли находитесь в имоголите, хотя исследования при помощи электронного спинового резонанса с использованием спиновых зондов не показали захватов малых органических молекул в трубках имоголита. Эти спиновые зонды в карбоксилированной форме показали, однако, электростатическое сохранение карбоксильных групп имоголитом и более специфическую адсорбцию аллофанами, включая лигандовый обмен поверхностных гидроксильных групп. Эти результаты указывают на врожденные различия в величинах заряда и свойствах поверхности аллофана и имоголита, несмотря на общую структурную единицу, которую оба минерала включают. [E.G.]

Resümee—Die negative Oberflächenladung von synthetischen Allophanen mit unterschiedlichen Si/Al-Verhältnissen nahm mit zunehmendem Al_2O_3 -Gehalt bei einem gegebenen pH ab, während die positive Ladung zunahm. Die Phosphatadsorptionskapazität nahm ebenfalls mit zunehmendem Al-Gehalt zu. Daß diese Beziehung zwischen Zusammensetzung und chemischer Reaktionsfähigkeit bei Boden-Allophanen nicht gefunden wurde, wird auf die Anwesenheit von spezifisch adsorbierten organischen oder anorganischen Anionen auf dem natürlichen Material zurückgeführt. Sowohl synthetische als auch natürliche Imogolite hatten eine viel niedrigere Phosphatadsorptionskapazität als die Allophane und adsorbierten ungewöhnlich große Mengen von Cl^- und ClO_4^- bei hohen pH-Werten. Es wird vorgeschlagen, daß in den Imogoliten ein Einbau von Salz auftritt, obwohl Elektronenspinresonanz-Untersuchungen mit Spinproben keine Einschlüsse von kleinen organischen Molekülen in den Imogolit-Röhren ergaben. Diese Spinproben in der karboxylierten Form deuteten jedoch auf eine elektrostatische Retention von Karboxylat durch Imogolit hin und auf eine mehr spezifische Adsorption durch Allophan, die einen Ligandenaustausch der Oberflächenhydroxyle mit einschließt. Diese Ergebnisse verdeutlichen die spezifischen Unterschiede bei der Ladung und den Oberflächeneigenschaften von Allophan und Imogolit trotz der gemeinsamen Struktureinheiten, die beide Minerale beinhalten. [U.W.]

Résumé—La charge de surface négative d'allophanes synthétiques avec une gamme de proportions Si/Al a diminué et la charge positive a augmenté lorsqu'on a augmenté le contenu en alumine à un pH donné. La capacité d'adsorption de phosphate a aussi augmenté lorsqu'on a augmenté le contenu en Al. On attribue à la présence d'anions organiques et inorganiques spécifiquement adsorbés sur le matériau naturel le fait que la même relation entre la composition et la réactivité chimique n'a pas été trouvée dans les allophanes de sol. Les imogolites synthétiques et naturels avaient tous deux une capacité d'adsorption de phosphate beaucoup plus basse que les allophanes, et avaient adsorbé des quantités anormalement élevées de Cl^- et de ClO_4^- à un pH élevé. On propose que l'intercalation de sel se produit dans l'imogolite, quoique le spin à résonance d'électrons utilisant des sondes de spin a manqué de révéler l'entrappement de petites molécules organiques dans les tubes d'imogolite. Ces sondes de spin dans la forme carboxylate ont cependant suggéré une rétention électrostatique de carboxylate par l'imogolite, et une adsorption plus spécifique par l'allophane impliquant l'échange ligand d'hydroxyles de surface. Les résultats illustrent les différences inhérentes dans les propriétés de charge et de surface de l'allophane et de l'imogolite malgré l'unité structurale commune que les deux minéraux incorporent. [D.J.]