

## SURFACE PROPERTIES OF ALLOPHANE, HALLOYSITE, AND IMOGOLITE

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**Abstract**—The adsorption of sodium, chloride, and phosphate ions by allophane, imogolite, and halloysite has been studied in relation to the surface structure of the mineral samples. The high adsorption of phosphate ( $>200 \mu\text{mole/g}$ ) and chloride ( $10\text{--}30 \text{ meq}/100 \text{ g}$  at pH 4) by allophane is ascribed to the small particle size of allophane, its high surface area ( $\sim 800 \text{ m}^2/\text{g}$ ), and the presence at the surface of Al-OH-Al groups and defect sites. In contrast, halloysite has a relatively large particle size and a Si-O-Si surface. Accordingly, the adsorption of phosphate ( $5\text{--}10 \mu\text{mole/g}$ ) and chloride ( $1 \text{ meq}/100 \text{ g}$ ) by halloysite is very much lower as compared with allophane. Phosphate adsorption by halloysite is also related to particle morphology and the number of edge sites. Thus, a sample consisting entirely of spheroidal particles adsorbed only  $5 \mu\text{mole/g}$  at a solution concentration of  $1 \times 10^{-4} \text{ M}$ , whereas the tubular types of comparable surface area adsorbed  $7\text{--}10 \mu\text{mole/g}$  at the same concentration. This is because spheroidal halloysite particles have few, if any, edge sites at which phosphate can adsorb. The relative degree of order and hydration of halloysite, as indicated by infrared spectroscopy, also affects phosphate adsorption. However, this factor is apparently less important than particle morphology and surface structure. Although imogolite also has an Al-OH-Al surface, it contains relatively few defect sites where phosphate can adsorb. Consequently, much less phosphate ( $120 \mu\text{mole/g}$ ) was adsorbed as compared with allophane.

**Key Words**—Adsorption, Allophane, Halloysite, Imogolite, Infrared spectroscopy, Phosphate, Surface charge.

### INTRODUCTION

Much of the North Island of New Zealand has received tephra deposits from eruptions of the Taupo and Okataina volcanic centers (Pullar *et al.*, 1973). The most massive eruptions in the last 50,000 years were those that gave rise to the rhyolitic Rotoehu and Kawakawa Tephra, dated at  $\sim 42,000$  and  $\sim 20,000$  years B.P., respectively. Small additions of andesitic tephra have also been received from the Tongariro and Egmont centers.

The tephra weathers to allophane, gibbsite, imogolite, and halloysite, with allophane and halloysite being the main products. Two forms of allophane have been identified, one having an Al/Si molar ratio of  $\sim 1.0$  and another in which this ratio is  $\sim 2.0$ . The latter form, which predominates, has been termed "proto-imogolite" allophane (Parfitt *et al.*, 1980) because it has the characteristic "proto-imogolite" infrared spectrum. However, all forms of allophane, irrespective of origin and chemical composition, have unit particles made up of hollow spherules with a diameter of  $35\text{--}50 \text{ \AA}$ . Because allophane and halloysite are common constituents of soils derived from volcanic ash, it seems desirable to examine the surface properties of these minerals and their reactivity towards anions and cations.

### MATERIALS AND METHODS

#### *Samples*

The allophane-rich sample from andesitic tephra, subsequently referred to as allophane-An was collected

from the 25–40-cm depth of an Egmont soil (20 km northwest of Wanganui, New Zealand) that was derived from tephra produced by Mt. Egmont. The material is similar to that designated SB 6674 by Fieldes and Schofield (1960). The allophane-rich sample from a rhyolitic tephra (allophane-Rh) obtained at a depth of 2 m, was derived from the Rotoehu Tephra in a section near Te Kuiti, New Zealand (grid reference N83/717612). "Silica Springs" allophane is a stream deposit from Silica Springs near Mt. Raupehu, New Zealand (Wells *et al.*, 1977), collected 190 m from the stream source. The imogolite sample, occurring as a gel film on pumice at Kurayoshi, Japan, was kindly provided by Professor N. Yoshinaga. The  $<2\text{-}\mu\text{m}$  fraction was separated from the gel by dispersion at pH 4 with an ultrasonic probe (100 watt, 10 min). The halloysites were collected from different localities in New Zealand: Opotiki halloysite (Opotiki, Bay of Plenty) formed from rhyolitic Pahoia Tuff (Kirkman, 1977); Te Puke halloysite ( $\sim 10 \text{ km}$  west of Te Puke) is a water-sorted deposit that probably formed by weathering and/or hydrothermal action in rhyolite and andesite (Hughes, 1966); Matauri Bay halloysite (Matauri Bay, Northland), formed from rhyolite and dacite by low temperature hydrothermal alteration (Marsters, 1978). The  $<2\text{-}\mu\text{m}$  fractions were separated by sedimentation under gravity; all samples were sodium saturated and washed free of excess electrolyte by either centrifugation or dialysis against distilled water. Synthetic gibbsite was prepared using the method described by Parfitt *et al.* (1977).

Table 1. Chemical analysis of samples using acid oxalate dissolution.

Lab. no.	Al (wt. %)	Si (wt. %)	Fe (wt. %)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (Molar)	Al/Si (Molar)	Al/Fe (Molar)
<i>Allophane samples</i>						
Andesitic tephra	959	11.6	6.2	3.5	1.02	1.95
Rhyolitic tephra	1037	22.1	14.6	2.5	1.27	1.57
Silica Springs	1013	27.3	15.6	0.1	1.10	1.80
<i>Imogolite</i>						
		25.0	13.1	1.8	1.01	2.0
<i>Halloysite samples</i>						
Opotiki	0.1	n.d.	n.d.			
Te Puke	0.2	0.1	n.d.			
Matauri Bay	0.3	0.3	n.d.			

n.d. = not detectable.

### Infrared spectroscopy

The air-dry clays were examined by infrared spectroscopy (IR) both in freshly prepared KBr disks (1:200) and after heating for 16 hr at 150°C, using a Pye Unicam SP200 spectrophotometer. Evacuation and D<sub>2</sub>O treatment were carried out in a vacuum cell on samples evaporated onto an AgCl sheet.

### Chemical analyses

Suspensions containing between 20 and 50 mg of clay were shaken in the dark with 25 ml of 0.15 M sodium oxalate (pH 3.5) at 20°C for 2 hr. The treatment dissolves allophane and imogolite but not halloysite (Higashi and Ikeda, 1974). Al and Fe in the extracts were determined by high-temperature emission spectroscopy, and Si by atomic absorption using a Techtron AA5 spectrophotometer.

### Phosphate adsorption

Phosphate adsorption was carried out by equilibrating portions of the suspension containing 10–25 mg of sample with the required amount of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> made up to 20 cm<sup>3</sup> with CaCl<sub>2</sub> solution and water so that the solution was 0.1 M with respect to CaCl<sub>2</sub>. The tubes were shaken for 16 hr, centrifuged, and phosphorus in the supernatant liquid was determined colorimetrically (Murphy and Riley, 1962). The final pH was between 4.5 and 6.0 for all samples.

### Charge characteristics and electron microscopy

The charge characteristics of the clays were determined by Schofield's (1949) method as modified by Perrott (1977) but using 0.05 M NaCl as the equilibrating solution and 0.1 M KNO<sub>3</sub> to displace the sodium and chloride ions from the system. Electron micrographs were obtained using a Philips EM 200 transmission electron microscope.

## RESULTS AND DISCUSSION

### Structure and morphology

The allophane-An sample has characteristics which closely resemble those of samples obtained from

another Egmont soil (Russell *et al.*, 1980). It has an Al/Si molar ratio of 1.95 (Table 1) and an IR spectrum (not shown) with bands at 348, 430, 550, and 950 cm<sup>-1</sup>, characteristic of "proto-imogolite" allophane (Parfitt *et al.*, 1980). Bands at 1100, 1030, 900, 800, and 470 cm<sup>-1</sup> indicate that glass and halloysite are also present. Their presence is confirmed by electron microscopy and differential thermal analysis (DTA) which indicate that the sample contains ~3% halloysite by weight. It contains 11.6% Al (Table 1) which, for "proto-imogolite" allophane is equivalent to approximately 50% allophane (Russell *et al.*, 1980). The remainder of the sample is made up of clay-size glass which is considered to be relatively inert.

The allophane-Rh sample is a mixture of "proto-imogolite" allophane (Al/Si = 2.0) and allophane with Al/Si = 1.0, together with traces of glass and imogolite (Parfitt *et al.*, 1980). Unlike soil allophane, the Silica Springs sample contains considerable (40%) aluminum in tetrahedral coordination (Parfitt and Henmi, 1980); structurally it is closer to feldspathoids than to soil allophane (Farmer *et al.*, 1979; Parfitt and Henmi, 1980).

Although these allophanes are structurally different, their morphology, as seen under the electron microscope, is remarkably similar in that all consist of small, hollow spherules with external diameters of 35 to 50 Å as reported by Henmi and Wada (1976) for Japanese allophanes. The imogolite sample was similar in form to that of other Japanese samples of this mineral (Wada, 1977).

The halloysites contain very small amounts of aluminum soluble in acid oxalate (Table 1) indicating the presence of only traces of allophane and poorly ordered material. The electron micrograph of the Opotiki sample shows that it consists of spheroidal particles with diameters between 4000 and 8000 Å. The Matauri Bay sample is largely made up of thick tubes 1000 Å in diameter and up to 20,000 Å long; the Te Puke sample consists mainly of relatively short tubular particles. The tubes are 400 Å in diameter and average 3000 Å in length.

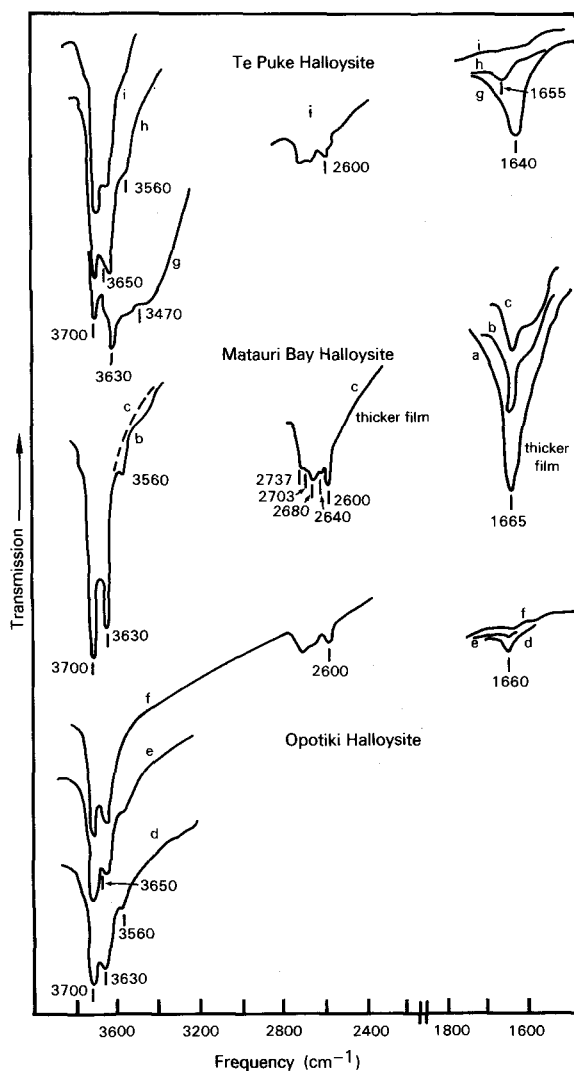


Figure 1. Infrared spectra of halloysite films: (a) Matauri Bay halloysite, (b) after evacuation, (c) after exposure to  $D_2O$  for 16 hr and then evacuated; (d) Opotiki halloysite, (e) after evacuation, (f) after exposure to  $D_2O$  for 16 hr and then evacuated; (g) Te Puke halloysite, (h) after evacuation, (i) after exposure to  $D_2O$  for 16 hr and then evacuated.

### Infrared spectroscopy

Figure 1 gives the IR spectra of the halloysite samples. All show three clear bands in the OH-stretching region, i.e., near 3700, 3630, and 3560  $cm^{-1}$ , together with a weaker band at 3650  $cm^{-1}$  (not seen in the spectrum of the Matauri Bay sample). By analogy with kaolinite (e.g., Rouxhet *et al.*, 1977), the strong bands at 3700 and 3630  $cm^{-1}$  may be assigned to surface and inner hydroxyl groups, respectively.

The OH groups responsible for the 3560- $cm^{-1}$  band were exchanged only slowly (16 hr exposure to  $D_2O$ )

with OD groups to give a band at 2600  $cm^{-1}$ . Persistence of the 3560- $cm^{-1}$  band (after evacuation for 1 hr) indicates that it arises from OH groups of adsorbed water which are not easily accessible. The sharpness of the band and its frequency suggest that this water has a unique environment and that it is not strongly hydrogen bonded. It probably exists as isolated pockets or "islets" that became entrapped in the interlayer space (Brindley, 1961) as the halloysite layers contracted on evacuation and dehydration.

After 16-hr exposure to  $D_2O$  some of the structural OH groups in halloysite exchanged to give bands near 2680, 2700, and 2735  $cm^{-1}$  (most clearly seen for the Matauri Bay sample, Figure 1c). These bands correspond to those near 3630, 3660, and 3700  $cm^{-1}$ , respectively, in the spectra of the nondeuterated samples. The 3650- $cm^{-1}$  band (Figures 1e and 1h), which is generally weak, was effectively removed by evacuation and  $D_2O$  treatment. These data suggest that the band near 3650  $cm^{-1}$  is due to surface OH groups.

There are differences between the three halloysites in the sharpness and relative intensity of the 3630- and 3700- $cm^{-1}$  bands. The degree of hydration of the samples affects these comparisons. In the initial spectrum (Figure 1g) of the Te Puke halloysite, which is also the most hydrated sample, the 3630- $cm^{-1}$  band is relatively broad and is more intense than the 3700- $cm^{-1}$  band. By contrast, both the Opotiki halloysite, which is partially dehydrated, and the Matauri Bay halloysite, which is largely dehydrated, have a stronger band at 3700  $cm^{-1}$  than at 3630  $cm^{-1}$ . In kaolinites, an intense 3700- $cm^{-1}$  band relative to the 3630- $cm^{-1}$  band is indicative of high crystallinity (Parker, 1969). The IR spectrum of the Matauri Bay halloysite together with X-ray powder diffraction data and DTA (unpublished) suggest that this sample is the most ordered of the three halloysites examined.

The IR spectra indicate that all three halloysites are hydrated. However, their interlayer water content is different, thus complicating comparisons of their crystallinities in terms of IR data alone. Measurements using different criteria show that these and other halloysite samples exhibit a range in crystallinity or degree of order.

### Charge characteristics

The adsorption of Na and Cl ions at different pHs is shown in Figure 2. The curves for allophanes and imogolite indicate the existence of pH-dependent positive and negative charges. Perrott (1977) reported similar results for soil allophanes. By contrast, the charge characteristics of halloysites show little variation with pH. The allophane samples adsorb  $\sim 20$  meq  $Na^+/100$  g at pH 8, suggesting that they contain approximately equal amounts of negatively charged sites, consisting largely of  $AlO^-$ ,  $AlOH^-$ , and  $SiO^-$  groups (Greenland and Mott, 1978). At pH 4 imogolite developed the most

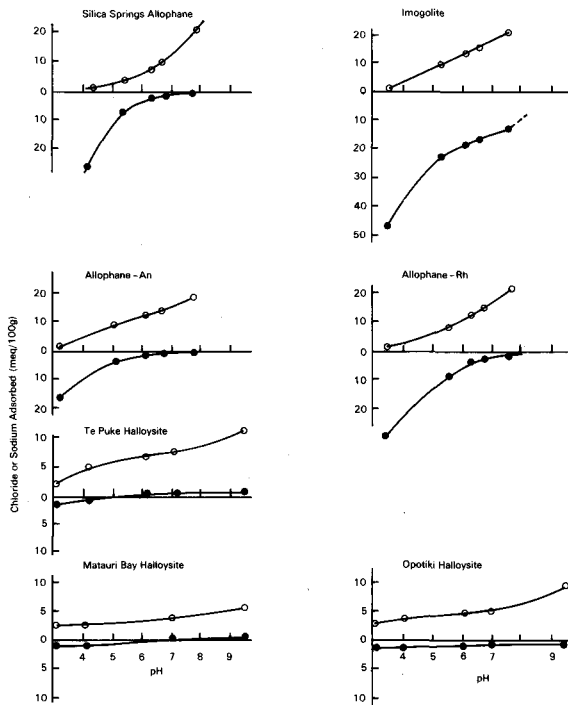


Figure 2. Adsorption of sodium (open circles) and chloride (solid circles) (from 0.05 M NaCl solutions) as a function of pH.

positively charged sites followed by Silica Springs allophane, allophane-Rh, and allophane-An, in that order. The Al content of the samples, extractable by acid oxalate, also follows the same order. For a surface area of 1450 m<sup>2</sup>/g (Wada, 1977) the charge density for imogolite at pH 4 can be calculated as one positive charge per 700 Å<sup>2</sup>, corresponding to approximately one charge for every 40 Al atoms. At the same pH, the allophane-Rh sample adsorbs 20 meq Cl/100 g, equivalent to approximately one charge per 65 atoms.

The halloysites developed a negative charge of 2–3 meq/100 g at pH 3, which is appreciably greater than that found for allophane and imogolite at a comparable pH. Bolland *et al.* (1976) showed that kaolinites have a permanent negative charge of about 3 meq/100 g which they ascribed to ionic substitution within the structure. By analogy, it seems likely that a similar process gave rise to a negative charge of this magnitude in halloysite, although edge Si-O<sup>-</sup> sites may also have contributed at pHs greater than 2 (Greenland and Mott, 1978).

An increase in negative charge beyond 3 meq/100 g, which developed when the suspension pH was raised, can be ascribed to deprotonation of water and hydroxyl groups bound to aluminum and silicon at crystal edges (Parfitt, 1980). This increase, which was greatest for the Te Puke halloysite and least for the Matauri Bay hal-

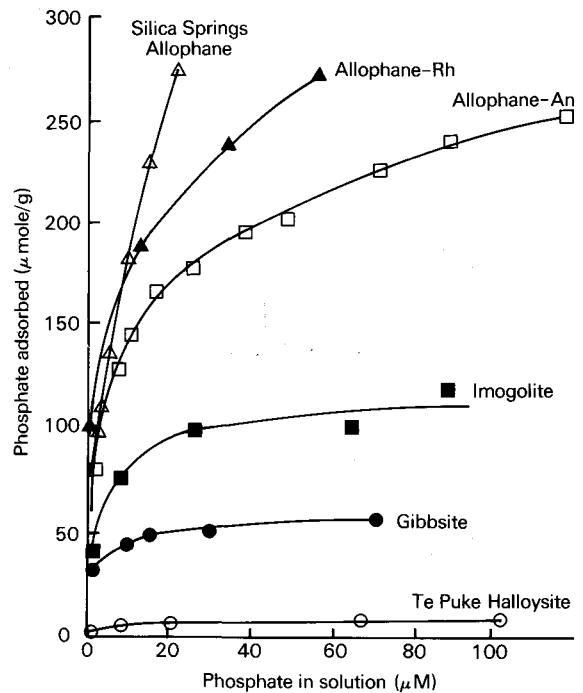


Figure 3. Phosphate adsorption curves in 0.01 M CaCl<sub>2</sub> (16-hr shaking time) for allophane, imogolite, gibbsite, and Te Puke halloysite samples.

loysite, appears to be related to a combination of particle morphology, hydration status, and crystallinity. The Te Puke sample, consisting of relatively short tubes and being hydrated (expanded), would have more edge sites at which deprotonation could occur as compared with the Matauri Bay sample which consists of thick long tubes which were dehydrated (contracted). The greater crystallinity of the Matauri Bay halloysite would also give rise to the lower pH-dependent negative charge as compared with the other halloysites. All of the halloysites developed little positive charge at low pH, and no positive charge was observed above pH 7; indeed, for the Matauri Bay and Te Puke samples chloride was negatively adsorbed at pH > 7.

Phosphate adsorption curves are shown in Figures 3 and 4. The allophanes have much greater adsorption capacities than the halloysites; the allophane-Rh sample adsorbed more than twenty times the amount of phosphate than the Te Puke halloysite. Significantly, the adsorption capacity of the allophanes at higher phosphate levels is directly related to the aluminum content of the samples. The allophane from the rhyolitic tephra adsorbed 120 μmole phosphate/g at a solution concentration of 1 × 10<sup>-6</sup> M. This value corresponds to approximately one phosphate ion per 400 Å<sup>2</sup>. Parfitt and Henmi (1980) suggested that allophane adsorbed phosphate at defect sites where broken bonds are exposed, giving rise to such groups as Al(OH)H<sub>2</sub>O.

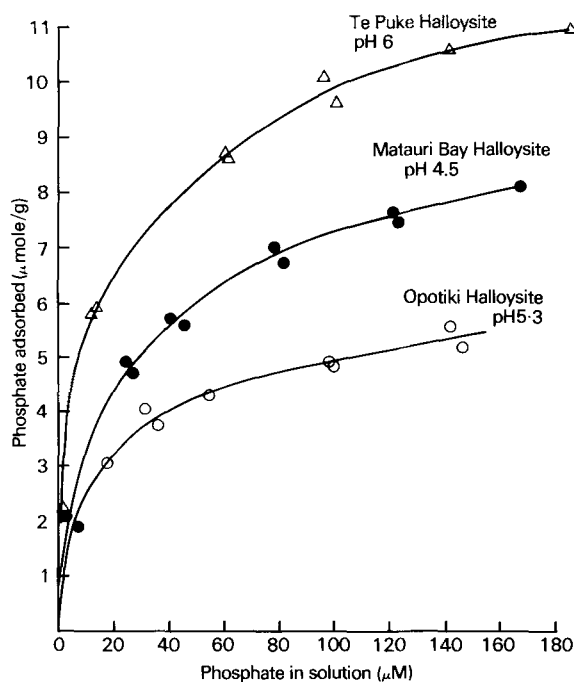


Figure 4. Phosphate adsorption curves in 0.01 M  $\text{CaCl}_2$  (16-hr shaking time) for halloysite samples.

Because these groups are protonated at low pH, they act as sites for anion adsorption.

Imogolite adsorbed less phosphate (Figure 2) but more chloride (Figure 1) than allophane for reasons which are not immediately apparent. It seems reasonable to suppose, however, that the "face" surface of imogolite tubes contains very few, if any defect sites where phosphate can adsorb. Defect sites would occur on tube ends and where individual tubes or bundles of tubes have been broken off (Wells *et al.*, 1980). It is at such sites that phosphate can adsorb, but because their number is small compared with allophane, the amount of phosphate adsorbed by imogolite is more restricted. On the other hand, chloride presumably adsorbed onto Al-OH-Al groups on the tube "faces" of imogolite when these groups became protonated at low pH. By analogy with gibbsite, phosphate ions are less likely to react with Al-OH-Al groups (Parfitt and Henmi, 1980). Because of its higher surface area, imogolite could adsorb more chloride than allophane at comparable (acid) pH values.

Halloysite adsorbed even less phosphate than imogolite (Figure 3). The Te Puke halloysite adsorbed 10  $\mu\text{mole/g}$  and the Matauri Bay and Opotiki samples only 7 and 5  $\mu\text{mole/g}$ , respectively, at  $1 \times 10^{-4}$  M phosphate in solution. On tubular halloysite, the sites for phosphate adsorption may be identified with AlOH groups, occurring largely on the tube ends (Parfitt, 1978). Because the Te Puke halloysite consists of shorter tubes

than the Matauri Bay sample, it has more adsorbing sites per unit surface and thus showed a higher adsorption capacity. By the same token, the spheroidal Opotiki halloysite should have only few, if any, edge sites except where defects occur, and its adsorption capacity was found to be accordingly low.

## CONCLUSIONS

Allophane, imogolite, and halloysite commonly coexist in volcanic ash soils. Their contrasting properties are related to their structure and morphology. Allophanes are composed of small hollow spherules with surface areas of approximately 800  $\text{m}^2/\text{g}$  (Parfitt and Henmi, 1980). Samples with Al/Si molar ratios close to 2.0 have a gibbsitic Al-OH-Al outer surface, and their surface properties appear to be related to defects in this surface. The chloride adsorption data indicate that on the average, one defect (site) exists per 650  $\text{\AA}^2$  giving rise to eight sites/spherule of 40  $\text{\AA}$  diameter (Parfitt and Henmi, 1980). Phosphate may also adsorb on such sites.

Imogolite has a tubular morphology and an external surface area of 1450  $\text{m}^2/\text{g}$ . Although imogolite develops a large positive charge (35 meq/100 g) at pH 4, as measured by chloride adsorption, no more than 12 meq phosphate/100 g (120  $\mu\text{mole/g}$ ) is adsorbed. These values are, respectively, higher and lower than those of allophane. The larger surface area of, and the fewer defect sites on imogolite as compared with allophane may account for the different reactivity of these two mineral species towards protons and phosphate.

Halloysites have surface properties which are related to particle morphology and the number of edge sites. The Opotiki halloysite consists of spheroidal particles (average diameter  $\sim 6000$   $\text{\AA}$ ) and thus has few, if any, edge sites at which phosphate can adsorb. Similarly, the low phosphate adsorption and small variable charge development of the Matauri Bay sample can be ascribed to its relatively high degree of crystallinity and large particle size. The Te Puke halloysite developed about 10 meq/100 g of pH-dependent negative charge; it adsorbed more phosphate and appeared to be less well-ordered than the other samples. All samples adsorbed 2–3 meq  $\text{Na}^+ / 100$  g at pH 3, indicating the presence of some permanent negative charge arising from ionic substitution.

Allophane has smaller unit particles than halloysite (40  $\text{\AA}$  compared with 6000  $\text{\AA}$ ). Moreover, halloysite tubes and spheroids have an Si-O-Si outer surface (Bates, 1959; Radoslovich, 1963) that is less reactive to phosphate than the Al-OH-Al surface exposed by allophane (with an Al/Si ratio of 2). These differences in surface properties between halloysite and allophane lie behind the observation that halloysitic soils have lower phosphate requirements than allophane-rich soils. The same is true for cation-adsorption properties, in that allophane takes up more cations than halloysite. Thus

at pH 6, ~10 meq Na/100 g is adsorbed by allophanes and only 5 meq/100 g by halloysites.

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**Резюме**—Исследовалась адсорбция ионов натрия, хлорида и фосфата на аллофане, имоголите и галлоизите по отношению к структурам поверхности образцов этих минералов. Высокая адсорбция фосфата (>200  $\mu\text{моль/г}$ ) и хлорида (10–30 экв/100 г при pH = 4) на аллофане приписывается малым размерам частиц аллофана, его большой площади поверхности (~800  $\text{м}^2/\text{г}$ ), а также присутствию групп Al–OH–Al на поверхности. В противоположность галлоизит характеризуется относительно большим размером частиц и Si–O–Si типом поверхности. Следовательно, адсорбция фосфата (5–10  $\mu\text{моль/г}$ ) и хлорида (1 экв/100 г) на галлоизите является низкой по сравнению с аллофаном. Адсорбция фосфата на галлоизите связана также с морфологией частиц и количеством краевых мест. Поэтому образец, состоящий исключительно из сфероидальных частиц, адсорбировал только 5  $\mu\text{моль/г}$  при концентрации раствора  $1 \times 10^{-4}$  M, тогда как образцы с частицами в виде таблиц со сравнимыми площадями поверхности адсорбировали 7–10  $\mu\text{моль/г}$  при этой концентрации. Это было результатом отсутствия, практически, краевых мест, на которых фосфат может адсорбироваться в сфероидальном галлоизите. Относительная степень упорядочения и гидратации галлоизита, определенная по инфракрасной спектроскопии, тоже влияет на адсорбцию фосфата. Однако, этот фактор является менее значительным, чем морфология частиц и структура поверхности. Хотя имоголит также имеет Al–OH–Al поверхность, он содержит относительно мало дефектов, на которых может быть адсорбирован фосфат. Поэтому меньшее количество фосфата (120  $\mu\text{моль/г}$ ) адсорбировалось имоголитом по сравнению с аллофаном. [Е.С.]

**Resümee**—Es wurde die Adsorption von Natrium-, Chlorid-, und Phosphat-Ionen durch Allophan, Imogolit, und Halloysit in Abhängigkeit von der Oberflächenstruktur der Mineralproben untersucht. Die Adsorption von Phosphat ( $>200 \mu\text{Mol/g}$ ) und Chlorid ( $10\text{--}30 \text{ mÄqu}/100 \text{ g}$  bei pH 4) durch Allophan ist durch die kleine Teilchengröße des Allophans und durch seine große Oberfläche ( $\sim 800 \text{ m}^2/\text{g}$ ), und durch die Anwesenheit von Al-OH-Al-Gruppen und Störstellen auf der Oberfläche bedingt. Halloysit hat im Gegensatz dazu eine relative große Teilchengröße und eine Si-O-Si-Oberfläche. Dementsprechend ist die Adsorption von Phosphat ( $5\text{--}10 \mu\text{Mol/g}$ ) und Chlorid ( $1 \text{ mÄqu}/100 \text{ g}$ ) durch Halloysit viel geringer im Vergleich zu der des Allophan. Die Phosphatadsorption durch Halloysit hängt ebenfalls mit der Teilchenmorphologie und der Zahl der Kantenplätze zusammen. Aus diesem Grund adsorbierte eine Probe, die nur aus kugelförmigen Teilchen bestand, nur  $5 \mu\text{Mol/g}$  bei einer Lösungskonzentration von  $1 \times 10^{-4} \text{ Mol}$ , während röhrenförmige Arten von vergleichbarer Oberfläche  $7\text{--}10 \mu\text{Mol/g}$  bei der gleichen Konzentration adsorbierten. Dies ist dadurch bedingt, daß die kugelförmigen Halloysitteilchen nur wenige, wenn überhaupt, Kantenplätze haben, an denen das Phosphat adsorbiert werden kann. Der relative Ordnungsgrad und Hydratationsgrad von Halloysit, der durch Infrarotspektroskopie zu erkennen ist, beeinflusst ebenfalls die Phosphatadsorption. Dieser Faktor ist jedoch offensichtlich weniger wichtig als die Teilchenmorphologie und die Oberflächenstruktur. Obwohl Imogolit ebenfalls eine Al-OH-Al-Oberfläche hat, enthält er relative wenig Störstellen, an die Phosphat adsorbiert werden kann. Demzufolge wurde viel weniger Phosphat ( $120 \mu\text{Mol/g}$ ) als an Allophan adsorbiert. [U.W.]

**Résumé**—On a étudié l'adsorption d'ions de sodium, de chlore, et de phosphore par l'allophane, l'imogolite, et l'halloysite, en relation avec la structure de surface des échantillons minéraux. L'adsorption haute du phosphore ( $>200 \mu\text{mole/g}$ ) et du chlore ( $10\text{--}30 \text{ meq}/100 \text{ g}$  à pH 4) par l'allophane est assignée à la petite taille de la particule maille de l'allophane, à sa grande aire de surface ( $\sim 800 \text{ m}^2/\text{g}$ ) et à la surface de groupes Al-OH-Al et de sites de défection. Par contraste, l'halloysite a une taille de particule relativement grande, et une surface Si-O-Si. Par conséquent, l'adsorption du phosphore ( $5\text{--}10 \mu\text{mole/g}$ ) et du chlore ( $1 \text{ meq}/100 \text{ g}$ ) par l'halloysite est beaucoup plus basse en comparaison avec l'allophane. L'adsorption de phosphore par l'halloysite est aussi apparentée à la morphologie de la particule et au nombre de sites sur les bords. Ainsi, un échantillon consistant entièrement de particules sphéroïdales n'a adsorbé que  $5 \mu\text{mole/g}$  à une concentration de solution d'  $1 \times 10^{-4} \text{ M}$ , tandis que les types tubulaires d'aire de surface comparable ont adsorbé  $7\text{--}10 \mu\text{mole/g}$  à la même concentration. Ceci se produit parce que les particules sphéroïdales d'halloysite n'ont que peu de sites sur les bords sur lesquels le phosphore peut être adsorbé, si en fait il y a de tels sites. Le degré d'ordre et d'hydratation de l'halloysite, indiqué par la spectroscopie infrarouge, affecte aussi l'adsorption de phosphore. Ce facteur est cependant apparemment moins important que la morphologie de la particule et que l'aire de surface. Malgré que l'imogolite a aussi une surface Al-OH-Al, elle contient relativement peu de sites de défection où le phosphore peut être adsorbé. Conséquentment, beaucoup moins de phosphore ( $120 \mu\text{mole/g}$ ) a été adsorbé en comparaison avec l'allophane. [D.J.]