STRUCTURE OF SOME ALLOPHANES FROM NEW ZEALAND

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Abstract—Allophane samples from soils, pumice, and stream beds have been studied by electron optical, infrared absorption, X-ray fluorescence, gas chromatography, and phosphate adsorption methods. The allophane particles were hollow spherules or polyhedra 35 and 50 Å in diameter with molar Al/Si ratios close to 2.0. The thickness of the wall of the spherules was estimated to be 7 Å. For the pumice allophanes, the wall was largely composed of imogolite structural units $(OH)_3Al_2O_3SiOH$. Defects or pores were present in the wall and probably were the sites where phosphate was adsorbed. It is suggested that these allophanes with molar Al/Si ratios close to 2.0 should be called "proto-imogolite" allophane.

Two soil allophanes had a similar structure to the allophane from Stratford pumice, but small amounts of layer silicates, including halloysite, were also present in the soil samples, as indicated by infrared bands at 470, 1030, and 1100 cm^{-1}. The allophane from the stream bed at Silica Springs had an infrared spectrum similar to feldspathoids, and it did not have the imogolite structure.

Key Words—Allophane, Crystal structure, Imogolite, Infrared spectroscopy, Phosphate adsorption, Volcanic ash.

INTRODUCTION

The name allophane has been used to describe a series of naturally occurring hydrous aluminosilicate clays characterized by short range order and by the predominance of Si–O–Al bonds (Wada, 1977). Recent high resolution electron micrographs of allophane samples separated from weathered volcanic ash and pumice showed that allophane was composed of hollow spherically shaped particles with diameters of 35–50 Å (Hemni and Wada, 1976; Wada and Wada, 1977).

Imogolite is also present in many volcanic ash soils and although it is a paracrystalline tubular mineral it has many properties in common with allophane including its infrared spectrum, thermogravimetric curve, X-ray powder diffraction lines at 2.25 and 3.3 Å, ready exchange of OH groups with D_2O, and a hollow structure (Wada, 1977). The atomic structure of imogolite (Cradwick *et al.,* 1972) and gives an ideal composition of $(OH)_3Al_2O_3SiOH$. Imogolite is used here as a model in the determination of the structure of some New Zealand allophanes.

MATERIALS AND METHODS

The samples were collected from the locations described in Table 1 and were stored in a moist condition in sealed plastic bags. The <2-μm fraction was extracted from the washed pumice samples 961 and 963, and sample 1013 by gently crushing, dispersing with an ultrasonic probe for 1 min at the pH given in Table 1 to obtain an adequate yield, and then centrifuging. The

<0.2-μm fraction was collected from samples 939 and 987 using the same dispersion treatment followed by centrifugation. The samples were saturated with Na using 0.1 M NaCl, the salts removed by dialysis against distilled water, and the samples stored as dilute suspensions. Imogolite (sample Ky G) was separated from gel which filled the interstices of the pumice beds at Kurayoshi, Japan. It was dispersed at pH 3.5, and the <2-μm fraction was collected by sedimentation and then saturated with Na. Synthetic gibbsite was prepared by the method described by Parfitt *et al.* (1977).

Chemical analysis

Suspensions containing about 20 mg of sample 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 dissolved allophane (Fey and Le Roux, 1977; Higashi and Ikeda, 1974), but left a trace of residue which was probably mainly glass. The suspensions (50 mg in 20 ml) were also treated with dithionite (0.2 g), sodium citrate (0.6 g), and sodium bicarbonate (2 ml, 1 M) at 90°C for 15 min. Al and Fe in the extracts were determined by high temperature emission spectroscopy and Si by atomic adsorption (AA) using a Techtron AA5 spectrophotometer.

Infrared spectroscopy (IR)

KBr disks, 13 mm in diameter, were prepared using 1.0 mg of air-dried sample and 200 mg of KBr. Evacuation and D_2O treatment (four times) was carried out
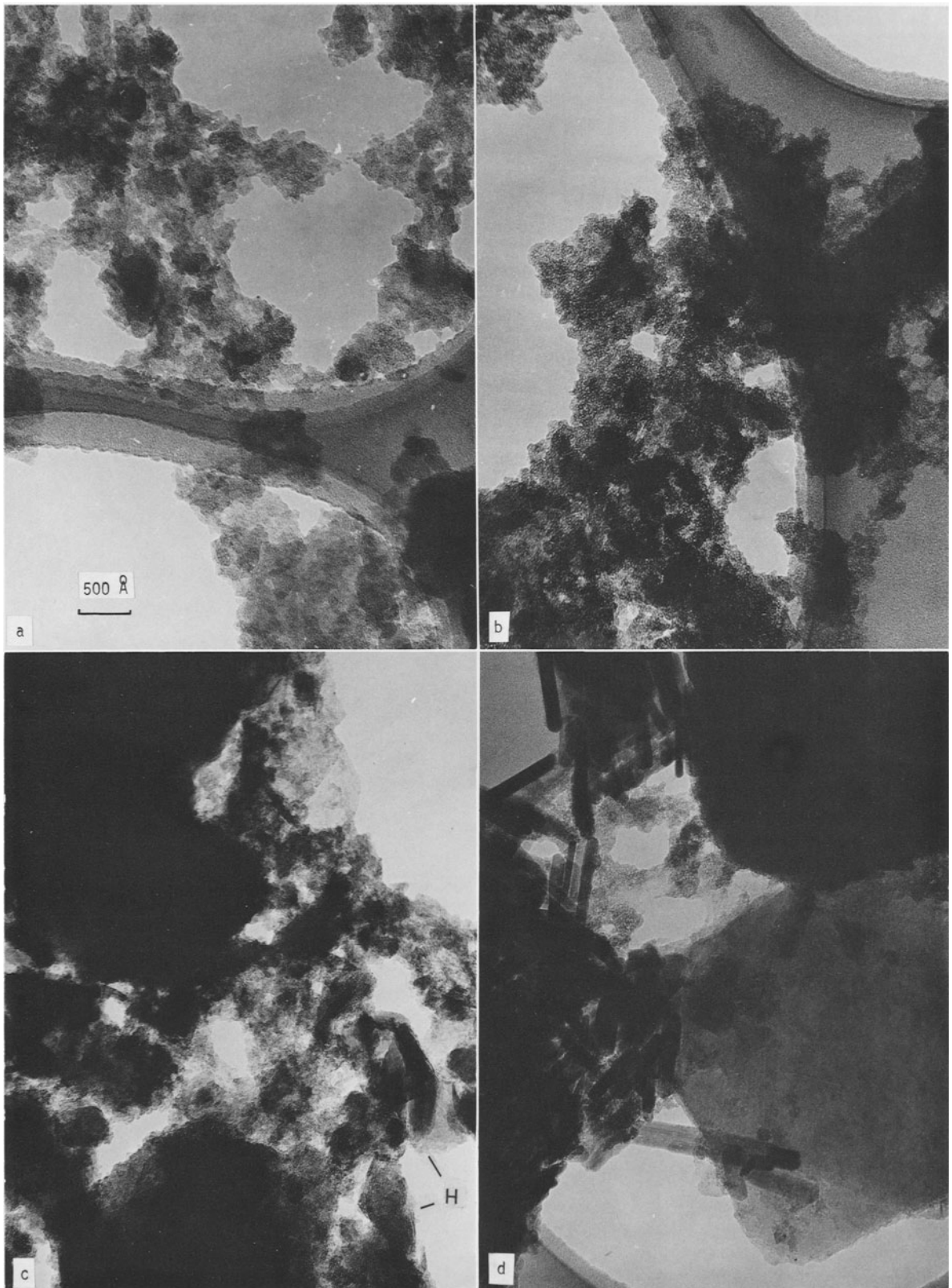
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Figure 1. Electron micrographs of (a) pumice allophane (961); (b) pumice allophane (963); (c) soil allophane and halloysite (H) (939); (d) soil allophane and halloysite (987).

Table 1. Origin of allophane samples and extraction pH.

Sample no.	Location (New Zealand)	Grid ref.	Parent material	Depth (cm)	Age BP (yr)	Tephra composition	Extraction pH
939	Mairoa soil	N82 497741	Mixed ash	69–94	~30,000	Mixed	6
961	Mt Egmont	N119 782596	Stratford pumice	140–150	~6000	Andesitic	10
963	Mt Egmont	N119 782596	Stratford pumice	170–180	~6000	Andesitic	4
987	Taupo soil	N85 803739	Taupo Ash	25–30	2000	Rhyolitic	10
1013	Mt Ruapehu[1]	N112 029729	Stream deposit	—	—	—	6

[1] Silica Springs deposit 190 m from source (Wells *et al.,* 1977).

on samples evaporated onto AgCl sheet. IR spectra were recorded between 200 and 4000 cm^{-1} on a Pye Unican SP200 spectrometer.

Phosphate adsorption

Phosphate adsorption was determined by equilibrating portions of the suspensions containing 10–25 mg sample with the required amount of $Ca(H_2PO_4)_2$ made up to 20 cm³ with $CaCl_2$ solution and water so that the solution was 0.01 M with respect to $CaCl_2$. The tubes were shaken for 16 hr, centrifuged, and the P in the supernatant liquid determined colorimetrically. The final pH was close to 5.8 for all samples.

Other techniques

X-ray fluorescence (XRF) was used to estimate the proportions of Al in tetrahedral and octahedral sites (Hemni and Wada, 1976). A PET crystal was used to analyze the AlKα line in a Siemens sequential XRF instrument. Synthetic gibbsite and zeolite 13X (obtained from British Drug Houses) were used as standards and the radiation was measured at 0.005°2θ intervals. A run contained two samples and the two standards; each run was repeated ten times.

The procedures for electron microscopy and gas chromatography of the trimethylsilyl ethers of silicates has been described previously (Henmi and Wada, 1976; Götz and Masson, 1970, 1971). Electron paramagnetic resonance (EPR) spectra were run at 298°K on a X-band Varian V4502 spectrometer using a frequency of 9.5 GHz and 30 mg of powdered sample.

The measurement of OH released from the sample by the reaction with NaF (0.85 M, pH 6.8, 25 min, 25°C) followed the procedure of Perrott *et al.* (1976). The measurement of acidity using Hammett indicators has been described by Henmi and Wada (1974). Differential thermal analysis (DTA) results were obtained using a Du Pont 900 differential thermal analyzer.

RESULTS

Electron microscopy and differential thermal analysis

The electron micrographs of samples 961 and 963 (Figure 1a, b) show that aggregates of small distorted

spheres or spherules are present, similar to those described by Henmi and Wada (1976). Where the small spherules are in focus, they appear to be hollow, with an external diameter of 35–50 Å, which is consistent with the descriptions of Japanese allophanes[1]. Wall thicknesses of the spherules are similar to those of the wall of imogolite tubes (<10 Å).

Samples 961 and 963 also contain some glass and imogolite which were estimated to be <5% of the sample. A few short tubes were observed, which were 50–100 Å in length, having the diameter of imogolite tubes. Electron diffraction examination of sample 963 revealed broad lines at 1.1, 1.4, 2.2, and 3.3 Å with the intensity increasing from very weak for the 1.1-Å line to strong for the 3.3-Å line.

Sample 939 (Figure 1c) is similar to samples 961 and 963 except that some halloysite-like material, similar to that described by Saigusa *et al.* (1978) in their Figure 6-1, is also observed. Sample 987 (Figure 1d) is also similar to samples 961 and 963 except for tubes approximately 800 Å in length and up to 200 Å in diameter which are probably one of the other morphological forms of halloysite found in volcanic ash soils (Saigusa *et al.,* 1978). The Silica Springs sample (1013) also has the characteristic ring shaped cross-section morphology of allophane as has been reported previously by Wells *et al.* (1977).

The DTA curves for samples 939, 961, 963, and 987 show strong endotherms near 100°C and exotherms near 900°C, characteristic of allophane, and weak inflections near 400°C, possibly due to imogolite. Samples 939 and 987 had additional very weak endotherms near 500°C, assignable to halloysite.

Infrared spectroscopy

The IR spectrum of sample 963 (Figure 2a) shows most of the usual features for allophane except that the band near 975 cm^{-1} is sharper than has been reported previously (Wada, 1977).

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[1] In this paper "allophane" refers to these spherules after Wada and Wada (1977), "imogolite" refers to the tubular mineral (Wada, 1977), and "imogolite structures" refers to the imogolite structural units $(OH)_3Al_2O_3SiOH$ on the atomic scale (Cradwick *et al.,* 1972).
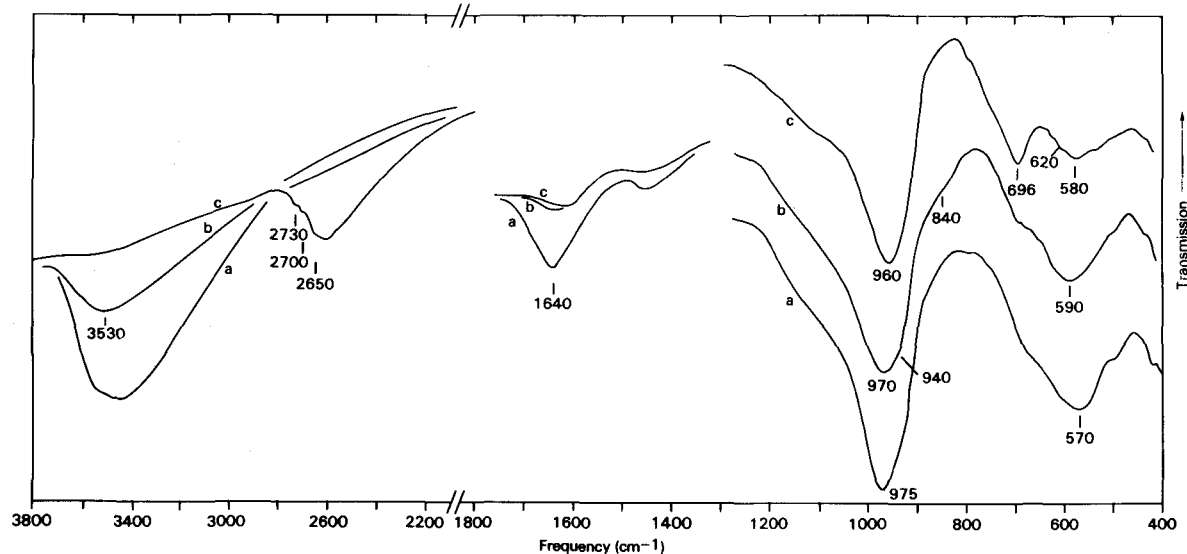
Figure 2.   Infrared spectrum of allophane 963 (a) in air; (b) evacuated 10 min; (c) treated with D_2O and evacuated 10 min.

1200–4000-cm⁻¹ region.   When sample 963 was evacuated (Figure 2b), the 1640-cm⁻¹ water band was largely removed, leaving bands near 1600 cm⁻¹ and 1460 cm⁻¹, due to organic impurities, and the OH-stretching adsorption at 3530 cm⁻¹. Comparison of the spectra (Figure 2a, b) in this region shows that most of the water can be removed by evacuation suggesting that it is not held strongly by allophane. Treatment with D_2O and evacuation removed the remaining water band at 1650 cm⁻¹ (Figure 2c).

The band at 3530 cm⁻¹ due to structural OH groups was largely removed by D_2O treatment, and an OD band appeared at 2600 cm⁻¹ with shoulders at 2650, 2700, and 2730 cm⁻¹. Thus, the large majority of structural OH groups were accessible to D_2O and exchanged rapidly, indicating an open structure for allophane. This is consistent with a hollow spherical morphology where the thickness of the spherical shell is <10 Å. The presence of OD-stretching vibrations at 2700 and 2730 cm⁻¹ indicated that two types of OD groups were in a free environment, and the other broad bands at 2600 and 2650 cm⁻¹ suggested that the bulk of the OH (OD) groups in the structure form hydrogen bonds over a wide energy range.

200–1200-cm⁻¹ region.   The spectrum of sample 963 (Figures 2 and 3b) has many of the features of the imogolite spectrum (Figure 3a), although the bands for sample 963 are generally broader. D_2O treatment produced a band at 696 cm⁻¹ (Figure 2c) assignable to SiOD corresponding to a SiOH vibration near 940 cm⁻¹ in Figure 2b (Cradwick *et al.*, 1972).

A band at 840 cm⁻¹ appeared when adsorbed water

was removed (Figure 2b) and then shifted to near 620 cm⁻¹ (Figure 2c) upon D_2O treatment. It is therefore assigned to an AlOH bending vibration (Cradwick *et al.*, 1972). The main Si–O–(Al) stretching vibration shifts from 975 to 960 cm⁻¹ during evacuation and D_2O treatment, consistent with an open structure for allophane. The Si–O stretching vibration at 970 cm⁻¹ (Figure 2b) is within the range for nesosilicates and sorosilicates (900–970 cm⁻¹) (Russell *et al.*, 1969).

The spectra of samples 961 and 939 treated with D_2O are very similar to the spectra for sample 963 (Figure 2) except that the absorbance of the AlOH band near 840 cm⁻¹ is stronger than that for sample 963 or imogolite, suggesting that more AlOH groups are present.

The spectra of samples heated at 150°C in KBr disks are shown in Figure 3. The spectra of the allophanes had bands at 348, 428, 500, 570, and 690 cm⁻¹, which were very close to the bands observed for imogolite (Figure 3a) (Farmer *et al.*, 1978). The 995-cm⁻¹ band due to the tubular morphology of imogolite (Figure 3a) was not observed for the allophane samples.

The absorbance of the band at 348 cm⁻¹ has been used to estimate the percentage of imogolite structural units in allophanes (Farmer *et al.*, 1977) (see Table 2). From these data 90% of sample 963 is made up of imogolite structures.

The spectrum of the stream sample 1013 (Figure 4a) was quite distinct from those of the tephra samples. The Si–O band at 1025 cm⁻¹ suggests that the silica is not present as a nesosilicate. The shoulder at 880 cm⁻¹ was observed in the presence of adsorbed water and did not shift after D_2O treatment. Therefore, it is not considered to be an imogolite-like AlOH vibration. However,
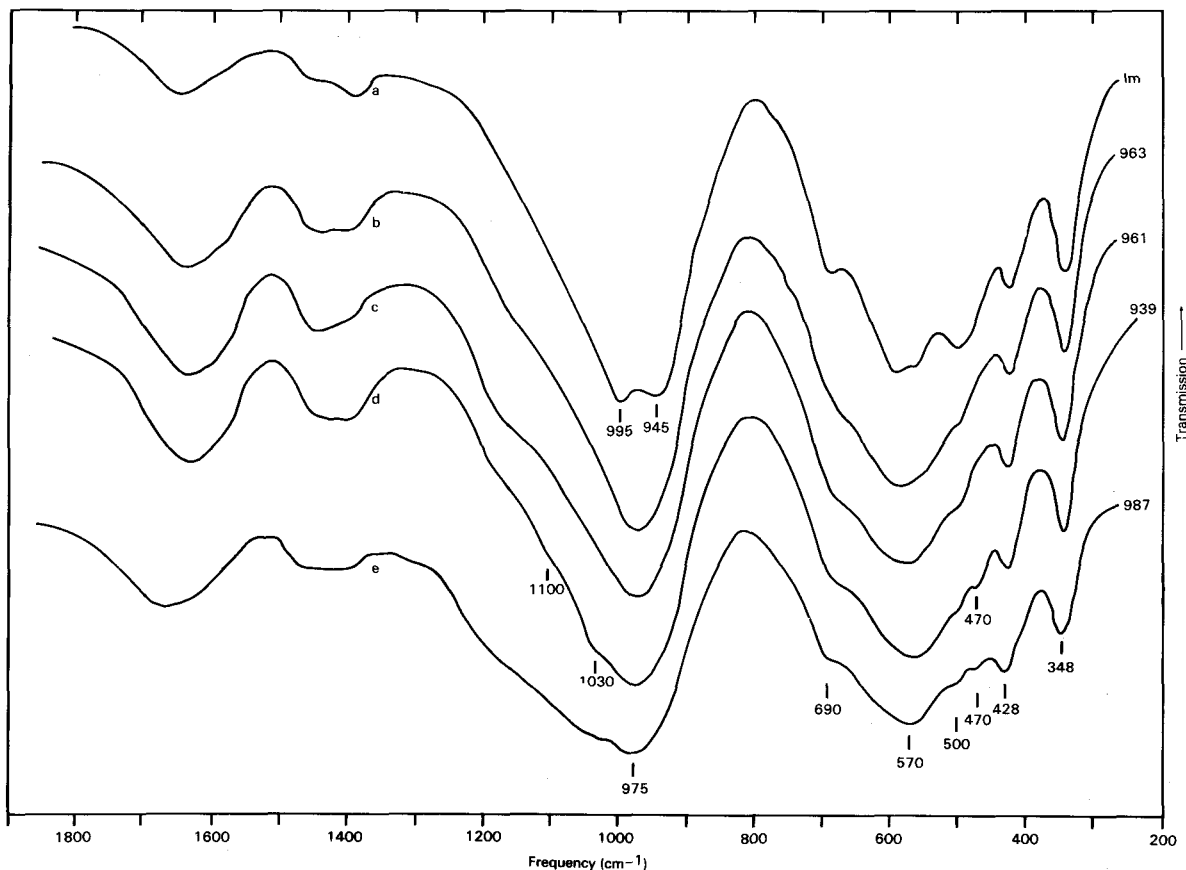
Figure 3.　Infrared spectrum of samples in KBr disks heated to 150°C (a) imogolite; (b) sample 963; (c) sample 961; (d) sample 939; (e) sample 987.

the appearance of a weak SiOD band at 700 cm^{-1} after D$_2$O treatment showed that some SiOH groups were present.

When the allophane samples were heated to 200°C,

Table 2.　Components of the allophane and imogolite samples.

Sample no.	Imogolite[1] structures (%)	AlOH[2] (μmole/ g)	OH released by NaF[3] (mmole OH/g)	$\left(\dfrac{Al^{IV}}{Total\ Al} \times 100\right)$[5]
939	85	320	27	0
961	85	320	34	0
963	90	320	37	0
987	65	160	27	—
1013	0	—	27	40
Imogolite	100	80	10 (17)[4]	0

[1] From infrared absorbance at 348 cm^{-1} (Farmer et al., 1977).
[2] Reactive AlOH groups by phosphate adsorption.
[3] From reaction with 0.85 M NaF, 25 min (Perrott et al., 1976).
[4] OH released after 50 min.
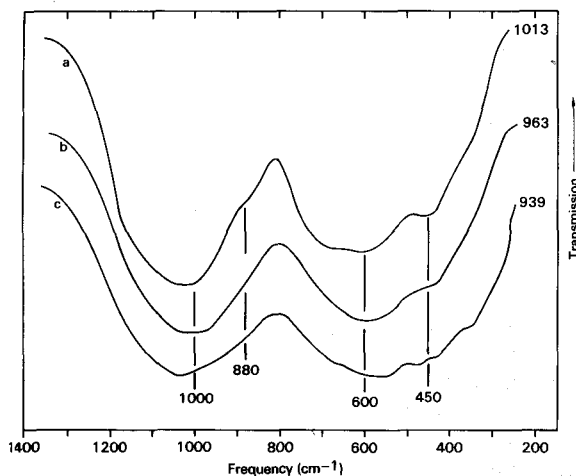[5] By X-ray fluorescence.

Figure 4.　Infrared spectrum of samples in KBr disks (a) Silica Springs allophane (sample 1013) 20°C; (b) pumice allophane (sample 963) heated to 280°C; (c) soil allophane (sample 939) heated to 280°C.

Table 3. Chemical analysis of allophane and imogolite samples.[1]

Sample no.	Acid oxalate extraction				Molar ratios					Dithionite-citrate-bicarbonate extraction			
	Al (%)	Si (%)	Fe (%)	H_2O+ (%)	SiO_2/Al_2O_3	Al/Si	Al/Fe	H_2O+/Al_2O_3	OH/Al	Al (%)	Si (%)	Fe (%)	Wt. loss (%)
939	21.6	9.3	6.6	26	0.85	2.3	7	3.6	3.6	5.0	0.7	5.7	33
961	23.1	10.5	3.6	23	0.87	2.3	14	3.0	3.0	4.2	1.1	2.3	27
963	25.6	13.3	4.0	22	1.00	2.0	13	2.6	2.6	4.5	1.1	2.9	30
987	17.1	8.8	3.4	22	1.01	2.0	10	3.8	3.8	—	—	—	—
1013	27.3	15.6	0.1	23	1.10	1.8	677	2.5	2.5	—	—	—	—
Imogolite[3]	25.0	13.1	1.8	—	1.01	2.0	30	—	—	0.5	0.5	0.3	—
Imogolite[4]	27.2	14.1	—	18.2	1.00	2.0	—	2.0	2.0	—	—	—	—

[1] On 150°C-dry basis.
[2] Loss between 150°C and 650°C.
[3] Kurayoshi sample.
[4] Ideal structure.

their spectra began to lose the imogolite-like features. These changes continued until 280°C, at which temperature broad features at 600 and 1000 cm⁻¹ with shoulders near 450 and 880 cm⁻¹ (Figure 4b, c) developed in the spectra. The shift in the Si–O band from 960 to near 1000 cm⁻¹ suggests that the SiO_4 tetrahedra became more polymerized. The spectra have some similarities with that of stream sample 1013 (Figure 4a) which suggests that tetrahedral Al sites (cf. Table 2) may be produced.

Comparison of weight losses at 150°, 280°, and 650°C indicates that the allophanes lost 70% of their structural OH at 280°C, and that clearly, the structures have become more polymerized. This is consistent with the shift in the Si–O band and formation of Al^{IV} sites.

When imogolite was heated to 280°C, the intensity of the imogolite bands was reduced but imogolite structures were still present. Thus, allophanes are less stable to heat treatment than imogolite, suggesting that allophanes are more disordered than imogolite.

Additional features appeared at 470, 1030, and 1100 cm⁻¹ in the spectra of the soil clay 939 (Figure 3d, 4c), and of sample 987 (Figure 3e). These features have been shown to arise from small amounts of halloysite and chlorite (Russell *et al.*, 1980) which generally are present in New Zealand volcanic ash soils.

When pyridine was adsorbed on imogolite and on the allophane samples, which had been treated with D_2O and evacuated, bands at 1440, 1485, and 1595 cm⁻¹ were observed, indicating that the pyridine was adsorbed on the allophane and imogolite surfaces by hydrogen bonding (Parfitt *et al.*, 1976). The pyridine was removed by evacuation showing that the hydrogen bonding was weak, a result which was also obtained for the goethite surface (Parfitt *et al.*, 1976). There was no evidence of a band near 1540 cm⁻¹ for samples prepared at both pH 3.5 and pH 6 suggesting that Bronsted ($Al^{IV}.OH_2^+$) acid sites either were not present on these allophanic samples or that they were not accessible to

pyridine molecules due to steric factors. A shoulder near 1610 cm⁻¹ indicated that Lewis acid sites ($Al.H_2O$) were present.

Chemical analysis

The elemental composition of the dissolved allophane and imogolite listed in Table 3 is expressed on a 150°C oven-dry basis because the IR results showed that the structures were stable up to this temperature. The water lost by drying between 105°C and 150°C was 5% of the mass at 150°C.

From these data sample 963 has the same Al/Si ratio as an ideal imogolite structure but its OH/Al ratio is higher suggesting that the allophane has a number of broken bonds where OH groups are exposed.

Samples 939 and 961 have higher Al/Si ratios consistent with their stronger AlOH IR adsorption near 840 cm⁻¹. Smaller amounts of Si and Al were extracted by acid oxalate from samples 939 and 987 since they contain insoluble clay minerals such as halloysite (see IR results).

All samples contained moderate amounts of Fe except for the stream sample 1013. Smaller amounts of Fe were extracted with dithionite than with acid oxalate. Acid oxalate dissolves disordered material such as allophane or protoferrihydrite, whereas dithionite completely dissolves iron-rich materials but only partially reacts with allophane (Wada, 1977). Therefore the allophane contains some acid oxalate-soluble Fe, which is not dissolved in dithionite, and the Fe is probably within the allophane structure substituting for Al.

Phosphate adsorption

Phosphate adsorption isotherms are shown in Figure 5. The isotherms were determined in 0.01 M $CaCl_2$ because, in this electroyte, strong adsorption occurs independent of pH. A standard shaking time of 16 hr was used; longer equilibration periods probably disrupt the structure of Al-containing adsorbents (Parfitt, 1978).
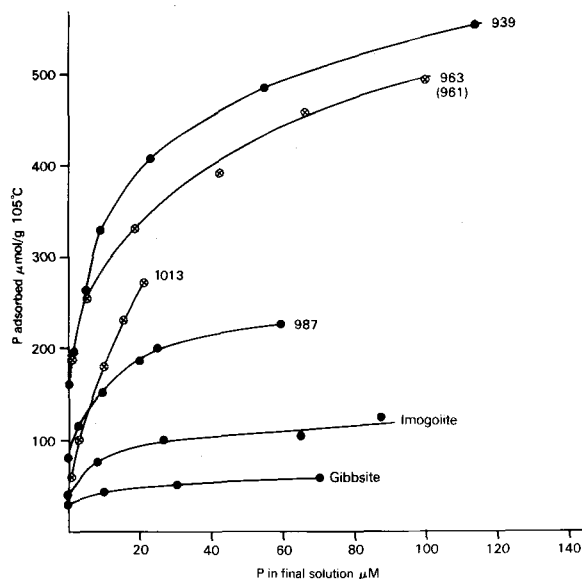
Figure 5. Phosphate adsorption isotherms (0.01 M $CaCl_2$, 23°C, pH 5.8, 16 hr).

Synthetic gibbsite is used here as a model for phosphate adsorption on surfaces containing AlOH groups. This gibbsite carries 60–70 μmole/g of reactive AlOH groups[2] which can react with small amounts of phosphate by a ligand exchange reaction (Parfitt *et al.*, 1977). The phosphate isotherm (Figure 5) showed that 30 μmole P/g adsorbed at low P concentration (1 μM P) and therefore twice this value corresponds to the number of reactive AlOH groups. This may be because, at this point on the isotherm where strong adsorption occurs, one phosphate ion reacts with two AlOH groups.

It is appropriate to use gibbsite as a model for phosphate adsorption on allophane and imogolite because a gibbsite-like sheet is present in imogolite structures. The number of reactive AlOH groups in allophane and

imogolite has been estimated from $2 \times P$ ads where P ads is the phosphate adsorbed at low P concentration (1 μM P in Figure 5). These estimates taken from Figure 5 are given in Table 2.

An alternative method of estimating reactive AlOH is to use a higher P ads value such as the apparent maximum adsorption value. However, this is difficult to estimate on Al surfaces because phosphate continues to react up to very high phosphate levels where another phase is formed (Parfitt, 1978).

The presence of Fe in the allophanes may influence phosphate adsorption, particularly if Fe is present as a separate phase in addition to Fe substituting for Al within the allophane structure. More phosphate is adsorbed by sample 939 than by sample 963 which may be because of the higher Fe content in sample 939.

The adsorption isotherm for stream sample 1013 is different from those of other samples (Figure 5). Lesser amounts of phosphate are adsorbed at low solution concentrations which is probably explained by the few AlOH groups (see IR results).

X-ray fluorescence and gas chromatography

Allophane samples 939, 961, and 963 gave XRF Al $K\alpha$ lines at angles which were close to those for gibbsite, and it was concluded that most of the Al was in octahedral sites. The peak angle for sample 1013 (147.34°) was intermediate between gibbsite (147.32°) and zeolite 13X (147.37°) giving an estimated 40% Al in tetrahedral sites (Table 2).

The gas chromatographs (see Table 4) of the imogolite and the allophane derivatives, with the exception of 1013, were similar to those obtained previously (Cradwick *et al.*, 1972). The chromatographic pattern for imogolite showed a higher percentage of the SiO_4 derivative than did olivine, a nesosilicate. The patterns for samples 939 and 963 were similar to olivine, whereas sample 1013 had a lower proportion of SiO_4 derivative and correspondingly higher percentages of the polymerized derivatives.

The absolute yield of extracted Si was low (~25%), but the similarities between the patterns of allophanes 939, 963, imogolite, and olivine may indicate that Si is present in these allophanes largely as independent SiO_4 tetrahedra. For sample 1013 the indication that the sil-

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[2] Reactive AlOH groups in gibbsite are the $Al^{VI}(OH)H_2O$ groups on edges where broken bonds occur and where the OH is co-ordinated to one Al ion only.

Table 4.   Si species as estimated by gas chromatography of trimethylsilyl ethers.

Sample	Area % in chromatogram				Wt. % Si extracted as			
	SiO_4	Si_2O_7	Si_3O_{10}	Si_4O_{12}	SiO_4	Si_2O_7	Si_3O_{10}	Si_4O_{12}
939	85	12	2	1	18.0	4.5	0.9	0.5
963	83	13	3	1	15.9	4.3	1.0	0.6
1013	68	23	6	3	12.0	6.9	2.3	1.6
Imogolite	92	7	1	0	29.0	3.7	1.0	0
Olivine	87	10	3	0	38.2	8.0	2.2	0

icate tetrahedra are more polymerized is consistent with the IR results.

Electron paramagnetic resonance (EPR)

The EPR spectra of the allophane sample 963 are very similar to those obtained by Kitagawa (1973), with bands near $g = 2$ and $g = 4$. The $g = 2$ band is assigned to high spin Fe^{3+} in an octahedral site and $g = 4$ to Fe^{3+} in a distorted octahedral site (W. C. Tennant, DSIR, Lower Hutt, New Zealand, personal communication). Sample 939 has a stronger signal at $g = 2$ due to the higher Fe content of this sample.

It seems likely that the Fe substitutes for Al in the allophane structure because no separate Fe phase was observed by the other techniques. However, an atomic coating of Fe on allophane particles or within aggregates would not be detected and this may also be present.

Dissolution in NaF and reaction to acidity indicators

Rapid reaction took place when NaF was added to the allophane samples, which indicates that there are a number of defect sites and broken bonds where F can react with Al and break up the structure. In contrast, imogolite reacted slowly because it is more ordered than allophanes and has less sites where F can attack the structure. The amount of OH released (Table 2) from the allophanes appears to be related to their Al content (Table 3), except for the stream sample 1013 which contains some Al^{IV}.

Sample 961 had a very low acidity, similar to that reported for imogolite. Samples 939 and 963 were very slightly more acid than imogolite. The acidity probably arises from specific sites where aluminum ions are held on the allophane surface. Such sites appear to be related to sites on kaolinite and montmorillonite (Henmi and Wada, 1974).

DISCUSSION

The electron micrographs showed that the samples consisted of many particles similar to the hollow spherules or polyhedra observed previously for allophane (Henmi and Wada, 1976; Wada and Wada, 1977). A small number of short tubes were present, and it is possible that some of the rings seen in the micrographs are the ends of tubes. However, the short tubes represented such a small proportion of the field that the majority of rings are almost certainly the images of hollow spherules, referred to here as allophane.

For sample 963, the IR results are similar to those obtained for imogolite (Russell *et al.,* 1969; Cradwick *et al.,* 1972). The bands assigned to SiOH and AlOH for imogolite occurred near 940 and 840 cm^{-1}, respectively (Figure 2), and the easy exchange of these groups with D_2O suggests that they are located on surfaces.

The appearance of several OD stretching vibrations, after evacuation, is similar to that found for imogolite, and the OD bands at 2700 and 2730 cm^{-1} show that in allophane also, some OD(OH) groups are not H-bonded.

The spectra of sample 963 and imogolite (Figure 3) are almost identical showing that the imogolite structure is present in this allophane sample. The absorbance of the band near 348 cm^{-1} was 90% of that of pure imogolite which suggests a high proportion of imogolite units in this allophane. This is supported by the XRF and gas chromatography data which show that the Si and Al in imogolite and allophane 963 are in similar environments and with chemical analysis which shows the Al/Si ratio in allophane 963 to be 2.0.

The Si–O–(Al) stretching mode of the isolated SiO_4 tetrahedra in imogolite occurred at 945 cm^{-1} in heated KBr disks, while for allophane 963 the band was at a somewhat higher frequency, 970 cm^{-1}, although still in the range expected for nesosilicates. The 995-cm^{-1} band of imogolite was not observed for the allophanes since it arises from the tubular morphology of imogolite.

The phosphate adsorption, NaF dissolution, IR spectra, and electron micrographs all indicate a lower degree of order in the allophanes than in imogolite. The imogolite structure is a single gibbsitic sheet, curled into a tube, with an outside diameter of 20 Å, and with O_3SiOH groups attached to the inside of the tube (Farmer and Fraser, 1979).

Allophane appears to have curved surfaces, and by analogy with imogolite the O_3SiOH groups must occur on the inside surface of a curled gibbsitic sheet. If the allophane particles are perfect spheres made up of imogolite units, 125 unit cells of imogolite would give the same surface area as a sphere 40 Å in diameter.

The phosphate adsorption results suggest that there are 320 μmole/g of reactive AlOH groups on sample 963. For a hypothetical perfect sphere, these sites could only be present if defects or pores occurred in the wall of the sphere, creating gibbsite-like edge sites.

Evidence for pores in the allophane spherule has recently been presented (Paterson, 1977; Wada and Wada, 1977), and the results suggest that the pore diameters are between 3 and 20 Å.

In Figure 6 two Si atoms and two Al atoms have been omitted from six imogolite unit cells (Cradwick *et al.,* 1972) to give a pore with a diameter of about 4 Å which could accommodate an orthophosphate ion. By making a number of assumptions it is possible to estimate the number of pores on each sphere. The assumptions are that allophane spheres have a diameter of 40 Å, a wall thickness of 7 Å with a density of 2.65 g/cm^3. This gives a specific surface of 800 m^2/g which contains 2×10^{21} unit cells/g or 13,000 μmole Al/g. If 320 μmole AlOH/g react with 160 μmole P/g and one phosphate adsorbs
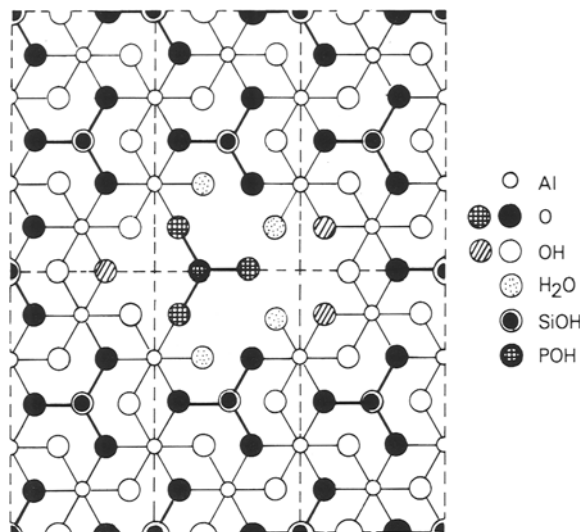
Figure 6. A model of "proto-imogolite" allophane showing a pore site and phosphate attached. The pore was created by omitting 2Si and 2Al from six imogolite unit cells.

on each pore, then there are six pores for each allophane sphere of 125 unit cells. This estimate is probably low because six of these pores would leave 95% of the surface with undistorted imogolite structures, and the IR results suggest this value is close to 90%.

The gas chromatography results indicate that sorosilicate (Si_2O_7) groups are present that may be adsorbed at pore sites or defect sites, preventing some phosphate ions from being adsorbed. Further evidence for additional defect sites comes from the H_2O/Al_2O_3 ratios for the allophanes. The ratio of 2.6 for allophane sample 963 would require more than 20 pores, of the type shown in Figure 6, per sphere. This large number of pores or defects would give the gibbsitic sheet the flexibility to form a distorted sphere.

The samples examined in this study were collected under humid moisture regimes (Cox, 1968) from both andesitic and rhyolitic tephras. The allophanes probably precipitated from weathering products of volcanic glass in an environment where hydroxyaluminum species and nesosilicates are produced. However, the imogolite units that formed are distorted and do not form tubes. It was noted (Table 3) that the iron content of allophanes is higher than that of imogolite and that the substitution of iron for aluminum in imogolite structures may induce a distortion which gives rise to the spherical morphology of allophane.

Samples 939 and 961 have higher Al/Si ratios and higher H_2O/Al_2O_3 ratios than sample 963 (Table 3), suggesting that some SiO_4 tetrahedra are absent in the imogolite units, leaving an occasional gibbsite-like structure in the allophane walls.

Investigations in this laboratory of 15 allophane sam-

ples obtained from soils or ash beds in New Zealand (e.g., samples 939, 987), always show contamination with small amounts of layer silicates (including halloysite) having distinctive IR bands at 470, 1030, and 1100 cm^{-1} which persist after heating the samples to 280°C (Figures 3 and 4, Farmer et al., 1978).

Stream sample 1013 has absorption bands, phosphate adsorption characteristics, Al^{IV} content, and silicate structures which are different from the other allophanes, and its properties are closer to aluminosilicate preparations which resemble feldspathoids (Farmer et al., 1979).

It is concluded, therefore, that the New Zealand allophanes which were formed from tephra have imogolite structures on the atomic scale but they do not exhibit the tubular morphology of imogolite. However, they do have distinctive shapes which in electron micrographs appear to be hollow spherules or polyhedra. These samples have IR spectra similar to synthetic "proto-imogolite" gels (Farmer et al., 1978, 1979; Farmer and Fraser, 1979). These data support the proposal of V. C. Farmer (Macauley Institute for Soil Research, Craigiebuckler, Aberdeen, Scotland; personal communication) that they be called "proto-imogolite" allophane.

ACKNOWLEDGMENTS

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Резюме—Образцы аллофана из почь, пемзы, и русел рек изучались методами электронной оптики, инфракрасной адсорбции, рентгеновской флуоресценции, газовой хроматографии, и фосфатной адсорбции. Аллофанновые частицы представляли собой полые сферы или многогранники с диаметрами 35 и 50 Å и молярными отношениями Al/Si, близкими к 2,0. Было установлено, что толщина стенок сфер пемзовых аллофанов равна 7,0 Å. Стенки в основном составлены из имоголитовных структурных элементов $(OH)_3Al_2O_3SiOH$. В стенках наблюдались дефекты или поры, которые вероятно служили местами адсорбции фосфатов. Предполагается, что эти аллофаны с молярными отношениями Al/Si, близкими к 2,0, должны называться «прото-имоголитовые» аллофаны.

Два почвенных аллофана имеют сходную структуру с аллофаном из Стратфордской пемзы, но небольшие количества слойных силикатов, включая галлуазиты, также присутствовали в почвенных образцах, что определяется инфракрасными полосами при 470, 1030, и 1100 см$^{-1}$. Аллофан из русла потока в Силика Спрингс имел инфракрасный спектр, подобный спектру фельдшпатойдов, и не имел имоголитовой структуры. [N.R.]

Resümee—Allophanproben aus Böden, Bims, und Flußbetten wurden mittels Elektronenoptik, Infrarotabsorption, Röntgenfluoreszenz, Gaschromatographie, und Phosphatadsorptionsmethoden untersucht. Die Allophanteilchen waren hohle Kügelchen oder Polyeder mit Durchmessern von 35–50 Å und einem molaren Al/Si-Verhältnis nahe 2,0. Die Dicke der Kugelwand wurde bei den Allophanen aus Bims auf etwa 7 Å geschätzt, wobei die Wand hauptsächlich aus Einheiten mit Imogolitstruktur $(OH)_3Al_2O_3SiOH$ bestand. Fehler oder Poren traten in den Wänden auf und waren wahrscheinlich die Stellen, wo Phosphat adsorbiert wurde. Es wird vorgeschlagen, diese Allophane mit molaren Al/Si-Verhältnissen nahe 2,0 als ''Proto-Imogolit'' Allophane zu bezeichnen.

Zwei Allophane aus Böden hatten eine Struktur ähnlich den Allophanen aus dem Stratford Bims, aber geringe Mengen von Schichtsilikaten einschließlich Halloysit waren in den Bodenproben enthalten, wie die Infrarotbanden bei 470, 1030, und 1100 cm^{-1} zeigen. Der Allophan aus dem Flußbett bei Silica Springs hatte ein Infrarotspektrum ähnlich dem von Feldspatvertretern und zeigte keine Imogolitstruktur. [U.W.]

Résumé—Des échantillons d'allophane de sols, de pierre ponce, et de lits de ruisseaux ont été étudiés par des méthodes optiques à électrons, d'adsorption infrarouge, de fluorescence aux rayons-X, de chromatographie de gaz, et d'adsorption de phosphate. Les particules d'allophane sont des sphérules creuses ou des polyèdres de 35 et 50 Å de diamètre avec des proportions molaires Al/Si près de 2,0. L'épaisseur de la paroi des sphérules était estimée être 7 Å, pour les allophanes de pierre ponce, la paroi était en grande partie formée d'unités structurales d'imogolite $(OH)_3Al_2O_3SiOH$. Des défauts ou des pores étaient présents dans la paroi et étaient probablement les sites d'adsorption de phosphate. On a suggéré que les allophanes avec des proportions molaires Al/Si près de 2,0 soient appellées allophanes ''proto-imogolite.''

Deux allophanes du sol avaient une structure semblable à l'allophane de la pierre ponce de Stratford, mais de petites quantités de silicates de couches comprenant de l'halloysite étaient aussi présentes dan les échantillons du sol, indiquées par les bandes infrarouges à 470, 1030, et 1100 cm^{-1}. L'allophane du lit de ruisseau à Silica Springs avait un spectre infrarouge semblable à celui des feldspathoides, et n'avait pas la structure de l'imogolite. [D.J.]