

IDENTIFICATION AND STRUCTURE OF TWO TYPES OF ALLOPHANE FROM VOLCANIC ASH SOILS AND TEPHRA

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Abstract—Samples containing allophane with molar Al/Si ratios from 1.0 to 2.0 have been examined by infrared spectroscopy, X-ray fluorescence, and phosphate adsorption methods. The infrared spectra of allophane with Al/Si ratios close to 2.0 showed that the wall of the allophane spherules is made up of imogolite structural units similar to "proto-imogolite." X-ray fluorescence gave no clear evidence of Al in tetrahedral sites (Al^{IV}), while pyridine adsorption results suggested that a small number of Bronsted acid sites ($Al^{IV}OH$) are present in silica-rich allophanes. Lewis acid sites (AlH_2O) are present in both silica-rich and alumina-rich allophanes. The results suggest that the framework for the allophane structure is an Al octahedral sheet.

Allophanes with Al/Si ratios close to 1.0 contain condensed silicate units either on the outside surface of the Al octahedral sheet, giving rise to a halloysite-like structure, or bonded on the inside surface of an imogolite-like structure. Allophanes with Al/Si ratios between 1.0 and 2.0 appear to be mixtures of the "proto-imogolite" structure and the allophane (Al/Si = 1.0) structure.

Key Words—Allophane, Deuterium exchange, Halloysite, Imogolite, Infrared spectroscopy.

INTRODUCTION

Allophane is the name given to a series of naturally occurring, hydrous aluminosilicate clays with Al/Si molar ratios between 1.0 and 2.0 (Wada, 1977). High resolution electron micrographs have shown that allophane separated from volcanic ash soils consists of hollow distorted spheres or polyhedra 35 to 50 Å in diameter (Henmi and Wada, 1976) with a wall thickness estimated to be about 7 Å (Wada, 1979). Wada and Wada (1977) suggested that the wall of the sphere consists of defect kaolin structures containing one octahedral (Al^{VI}) sheet and one tetrahedral (Si, Al^{IV}) sheet, and Wada (1979) proposed structural formulae for two end members of the allophane series. Both of these proposed end members contain tetrahedral sheets with Al substituting for Si in one-third of the cation sites. The octahedral sheet of the end member with Al/Si = 1.0 is not continuous; two-thirds of the possible octahedral sites are vacant, suggesting that the tetrahedral sheet provides the framework of the structure.

Parfitt and Henmi (1980) showed that some New Zealand allophanes with Al/Si ratios close to 2.0 are composed of distorted imogolite structures that can be described as "proto-imogolite allophane" (V. C. Farmer, Macauley Institute for Soil Research, Craigiebuckler, Aberdeen, Scotland; personal communication). In these samples no Al in tetrahedral sites was detected, and the octahedral (gibbsitic) sheet provided the structural framework. Farmer *et al.* (1979) used infrared

spectroscopy to investigate a Japanese allophane with a low Al/Si ratio and suggested that the structure had similarities with that of halloysite.

In this paper allophanes with a range of compositions have been studied using infrared spectroscopy in conjunction with D_2O treatment in an attempt to elucidate the structure of the allophane series.

MATERIALS AND METHODS

The tephra samples, described in Table 1, were stored in a field-moist condition in sealed polythene bags. A fine (allophane-containing) fraction (Table 1) was separated from the lapilli (pumice) samples by washing the lapilli to remove any imogolite surface coating, and then crushing, dispersing at the required pH with an ultrasonic probe, and centrifuging to obtain an adequate yield. The ash samples from volcanic ash soils were treated in a similar manner except that the washing step was omitted.

The experimental methods for electron microscopy, infrared spectroscopy (IR), X-ray fluorescence (XRF), and chemical analysis were described previously (Parfitt and Henmi, 1980).

RESULTS

The Al, Si, and Fe contents of the allophanes, determined by dissolution of the samples in acid oxalate and subsequent analysis of the solution, are given in Table 2. The Al/Si molar ratios ranged from 1.07 for sample

Table 1. Origin of allophane samples.

Sample	Size fraction	Location	Tephra	pH (H ₂ O)	Pretreatment for dispersion
KnP1	<0.4 μm	Kakino, Kyushu ¹	As-d ³ lapilli (Andesitic)	5.5	H ₂ O ₂
KnP2	<0.4 μm	Kakino, Kyushu ¹	As-d ³ lapilli (Andesitic)	5.5	pH 7
1034	<0.5 μm	Rotorua, N.Z. ²	Waiohau Ash (Rhyolitic)	5.9	pH 10
1035	<0.5 μm	Rotorua, N.Z. ²	Tsg 19 ash (mixed)	5.9	pH 10
1037	<2 μm	Te Kuiti, N.Z. ³	Tephric loess (at 2 m) (mixed)	6.1	pH 4
963	<2 μm	Mt Egmont, N.Z. ⁴	Stratford lapilli (Andesitic)	5.9	pH 4

¹ Tamura (1967).

² Goh and Pullar (1977).

³ Grid reference N83/717612.

⁴ Parfitt and Henmi (1980).

KnP1 to 2.00 for sample 963. The percent Al extracted by acid oxalate is a guide to the purity of the samples, e.g., sample 963 contains 25.6% Al, and "pure" imogolite contains 27.2% Al (Parfitt and Henmi, 1980), indicating that sample 963 is about 95% allophane.

Electron microscopy showed that the samples were composed largely of distorted spheres or polyhedra characteristic of allophane separated from volcanic ash and lapilli or pumice (Henmi and Wada, 1976). All samples contained traces of volcanic glass and short imogolite tubes. The KnP samples also contained traces of spherical or spiral halloysite particles.

The IR spectra of the allophane samples prepared in KBr disks and heated to 150°C are given in Figure 1. The Si-rich allophane (sample KnP1) has an absorption maximum at 1020 cm⁻¹, while the Al-rich allophane (sample 963) has an absorption maximum at 975 cm⁻¹. The other allophanes have absorption maxima which

appear to be composed of both 975 and 1020 cm⁻¹ components. The bands at 580 cm⁻¹ and 680 cm⁻¹ (Figure 1) are common to all the samples and are associated more with vibrations of Al octahedra than of Si tetrahedra (Farmer *et al.*, 1979) and probably arise from an octahedral sheet similar to the gibbsitic sheet present in imogolite structures (Cradwick *et al.*, 1972). The absorbance at 348 cm⁻¹ decreased as the Al/Si ratio decreased from sample 963 to sample KnP1. The absorbance of this band was used (Table 2) to estimate the percentage of imogolite structure units in these samples (Farmer *et al.*, 1977).

The intensity of the band near 430 cm⁻¹ also decreased as the Al/Si ratio decreased. This band is well developed for imogolite and "proto-imogolite" (Farmer and Fraser, 1979; Farmer *et al.*, 1979; Parfitt and Henmi, 1980), and it is also present in halloysite and kaolinite spectra. However, the band at 470 cm⁻¹ is more

Table 2. Chemical analysis of allophane samples.¹

Sample	Al (wt. %)	Si (wt. %)	Fe (wt. %)	H ₂ O(+) (wt. %)	SiO ₂ /Al ₂ O ₃ (molar)	Al/Si (molar)	Al/Fe (molar)	H ₂ O(+)/Al ₂ O ₃ (molar)	Imogolite ³ structure (%)
Kaolinite ²	20.9	21.7	—	14.0	2.00	1.00	—	2.0	—
KnP1	16.4	15.8	4.3	13.7	1.86	1.07	8	2.5	27
KnP2	16.7	14.0	3.6	14.7	1.62	1.23	9	2.6	27
1034	20.2	13.9	4.4	27.7	1.32	1.52	9	4.1	63
1035	19.0	12.4	4.9	28.6	1.30	1.54	8	4.5	52
1037	23.1	15.3	2.6	17.1	1.27	1.57	18	2.2	70
963	25.6	13.3	4.0	23.0	1.00	2.00	13	2.6	90
Imogolite ²	27.2	14.1	—	18.0	1.00	2.00	—	2.0	—

¹ By acid-oxalate dissolution, on 150°C oven-dry basis.

² Ideal structure.

³ From infrared absorbance at 348 cm⁻¹.

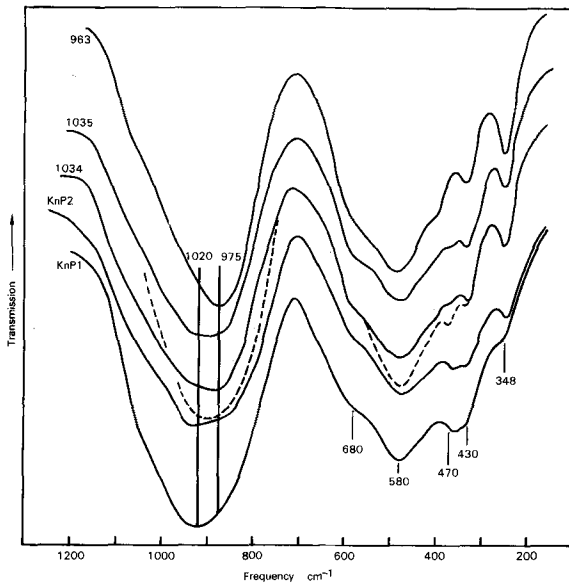


Figure 1. Infrared spectrum of samples in KBr disks heated to 150°C. (a) sample 963, Al:Si = 2.00, (b) sample 1035, Al:Si = 1.54, (c) sample 1034, Al:Si = 1.52, (d) sample KnP2, Al:Si = 1.23, (e) sample KnP1, Al:Si = 1.07. Dashed line is sample 1037, Al:Si = 1.57.

strongly developed for halloysite and other layer silicates and volcanic glass (Farmer *et al.*, 1977) and probably arises from Si-O and Al^{IV}-O tetrahedral bending vibrations (Flanigen *et al.*, 1971; Flanigen, 1976). This band was observed for the allophane samples of intermediate composition. The band for sample KnP1 appeared to be centered near 450 cm⁻¹.

The spectra for samples KnP1 and KnP2 prepared as films on AgCl sheets and evacuated and treated with D₂O are given in Figures 2a-2c and 3a-3c. Bands near 840, 940, and 950 cm⁻¹ have been assigned previously to AlOH, SiOH, and "proto-imogolite" SiO(Al) vibrations, respectively (Parfitt and Henmi, 1980). The band at 1020 to 1040 cm⁻¹ is assignable to a condensed silicate phase similar to halloysite (Farmer *et al.*, 1979).

On D₂O treatment the 840 cm⁻¹ AlOH band shifts to give an AlOD band near 620 cm⁻¹, and the 940 cm⁻¹ SiOH band shifts to give the SiOD equivalent near 690 cm⁻¹ (Cradwick *et al.*, 1972; Parfitt and Henmi, 1980). An alternative assignment (Wada, 1966) ascribes the stronger 840 cm⁻¹ and 690 cm⁻¹ bands to AlOH and AlOD respectively, giving a low isotope ratio of 1.22, and neglects the 940 cm⁻¹ and 620 cm⁻¹ shoulders.

The spectra in the 1300 to 4000 cm⁻¹ region (not shown) were similar to spectra reported previously (Parfitt and Henmi, 1980). The structural OH groups exchanged readily with D₂O, and for sample KnP1 a broad band was observed near 2600 cm⁻¹ with shoulders near 2700 and 2750 cm⁻¹. The ready exchange of structural OH groups is consistent with a thin sheet

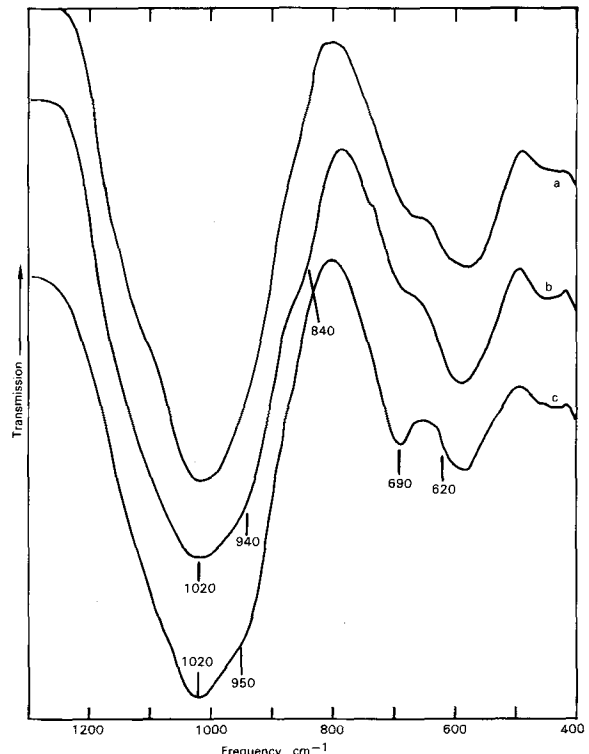


Figure 2. Infrared spectrum of sample KnP1 Al:Si = 1.07 (a) in air, (b) evacuated 20 min, (c) treated with D₂O and evacuated 20 min.

structure for allophane, such as the wall of a spherule about 7 Å thick (Wada and Wada, 1977).

The spectra of D₂O-treated sample 963 were given previously (Parfitt and Henmi, 1980). The band near 960 cm⁻¹ was reported to be very sharp and to indicate a well-ordered structure which was identified as "proto-imogolite." No shoulder was observed near 1020 cm⁻¹. The 975 cm⁻¹ band¹ (Figure 1) decreased in intensity as the Al/Si ratio decreased for the allophane samples until for sample KnP2 it appears as a shoulder, whereas the band near 1020 cm⁻¹ increased as the Al/Si ratio decreased. This latter band is well developed in sample KnP1 (Figure 2), but it appears as a medium intensity shoulder in samples 1034, 1035, and 1037 (Figure 4).

The clear resolution of the two bands near 950 and 1020 cm⁻¹ for sample KnP2 (Figure 3c), and shoulders for samples 1034, 1035, and 1037 (Figure 4), suggest that intermediate members of the allophane series are mixtures of two types of allophane rather than intermediate structures. Intermediate structures would have given one broad band with a maximum between 950 and 1020 cm⁻¹, the exact frequency being a function of the Al/Si ratio.

¹ This "proto-imogolite" band appears near 975 cm⁻¹ in KBr disks and near 950 cm⁻¹ for D₂O treated films.

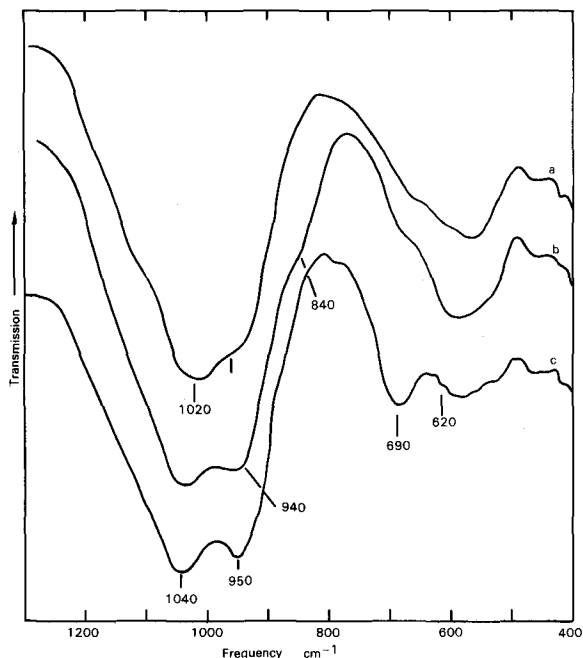


Figure 3. Infrared spectrum of sample KnP2, Al:Si = 1.23 (a) in air, (b) evacuated 20 min, (c) treated with D₂O and evacuated 20 min.

The increased resolution of the 950 cm⁻¹ and 1020 cm⁻¹ SiO(Al) and SiO(Si) bands after D₂O treatment of sample KnP2 (Figure 3) is partly due to the shift of the SiOH and AlOH bands from this region to lower frequencies, a result of the increased mass of OD groups affecting the vibrations of the whole open structure, and possibly also due to the removal of adsorbed H₂O. For "proto-imogolite" the structural formula is (OH)₃Al₂O₃SiOH which becomes (OD)₃Al₂O₃SiOD after D₂O treatment. Thus it is not surprising that the SiO(Al) bands near 1000 cm⁻¹ also shift on D₂O treatment.

The IR spectra of pyridine adsorbed in a vacuum cell on sample KnP2 and dried at both pH 9.5 (with NaOH) and pH 3.5 (with HCl) show bands at 1445, 1490, and 1595 cm⁻¹ (Figure 5) due to pyridine that is H-bonded to the allophane surface, and a shoulder at 1610 cm⁻¹ assignable to pyridine adsorbed at Lewis acid sites (AlH₂O → Alpy) Parfitt *et al.*, 1976). A very small inflection near 1550 cm⁻¹ suggests that a very small number of Bronsted acid sites (Al^{IV}OH₂⁺) may be present (see Ward, 1976).

XRF spectroscopy, which was carried out in a vacuum to remove adsorbed water, implied that Al is almost completely in octahedral (Al^{VI}) sites because the AlK α peak positions for all samples were close to that for gibbsite (Al^{VI}), whereas the position of this peak for zeolite X (Al^{IV}) is at a significantly higher angle.

Phosphate adsorption data showed that adsorption

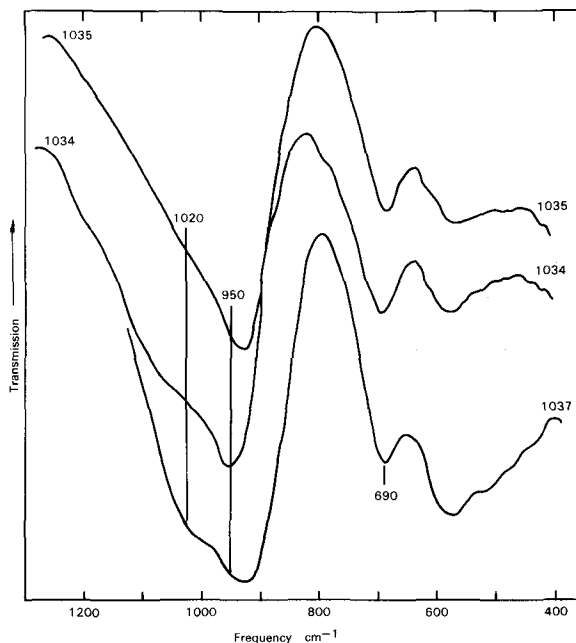


Figure 4. Infrared spectrum of samples 1035 (Al:Si = 1.54), 1034 (Al:Si = 1.52), and 1037 (Al:Si = 1.57) treated with D₂O and evacuated 20 min.

increased as the Al/Si ratio of allophane increased (Figure 6). Phosphate adsorption occurs by ligand exchange of active AlOH groups, and thus sample 963 has more accessible active AlOH groups than sample KnP2, with sample 1037 having an intermediate number of groups. The level of phosphate adsorption may be related not only to the different structures but also to different types of defect in these allophanes (Parfitt and Henmi, 1980).

DISCUSSION

Having an imogolite structure on the atomic scale (Parfitt and Henmi, 1980), sample 963 provides a reference point within the allophane series. This clay has an Al/Si molar ratio of 2.0, short range order, an IR spectrum similar to "proto-imogolite," and unit particles that appear to be hollow spherules, 35–50 Å in diameter. The allophane series is thought to extend from Al/Si molar ratios of 2.0 to 1.0, although ratios as high as 2.5 have been reported (Wada, 1977). The results presented here show that all the samples have IR spectra with similarities to sample 963. However, the intensities of the 975 cm⁻¹ and 348 cm⁻¹ bands decrease as the Al/Si ratio decreases, while new bands at 1020 cm⁻¹ and 470 cm⁻¹ increase in intensity. A model for the allophane series must explain these results together with the phosphate-adsorption results, the acidity data of Henmi (1977), the charge characteristics reported by Wada and Okamura (1977) and Greenland and Mott (1978), and the spherical morphology (Henmi and Wada, 1976).

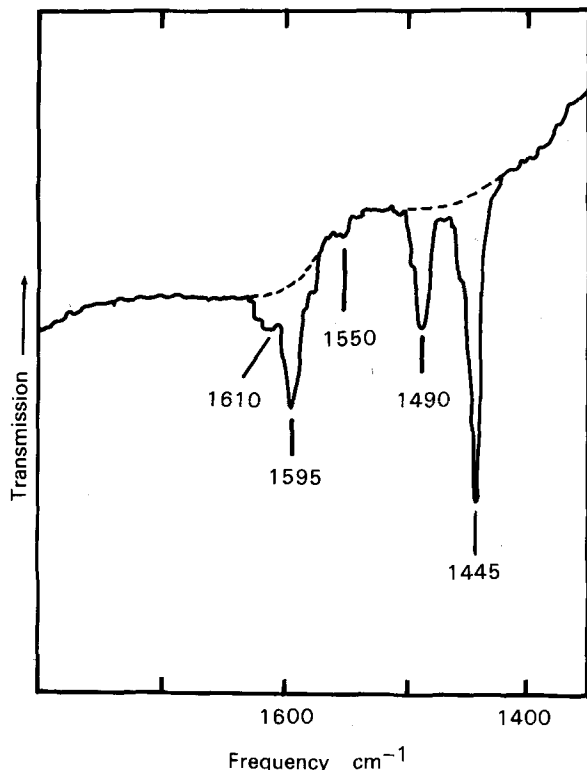


Figure 5. Infrared spectrum of pyridine adsorbed on sample KnP2 (pH = 3.5).

If allophanes with molar Al/Si ratios close to 1.0 have a structure that approaches halloysite (Farmer *et al.*, 1979), where the condensed silicate sheet is at the outer curved surface and the Al octahedral sheet is at the inner curved surface (Bates, 1959; Radoslovich, 1963), the results could be explained as follows: (1) the acidity is high because it is a characteristic of the halloysite surface (Henmi and Wada, 1974); (2) the phosphate adsorption is low because the active AlOH is on the internal surface; and (3) the positive charge is low because active AlOH sites, which become AlOH_2^+ at low pH, are not exposed and the charge either does not develop or cannot be measured.

If the halloysite model is correct for samples with Al/Si = 1.0 the allophane must contain defects to account for: (1) the low radius of curvature of allophane; (2) the weakness of the 348 cm^{-1} , 430 cm^{-1} , and 470 cm^{-1} bands; (3) the shift of the 540 cm^{-1} and 910 cm^{-1} bands; and (4) the penetration of deuterium to the inner OH sites. This halloysite model requires that the 690 cm^{-1} OD band (Figures 2–4) be assigned to AlOD (Wada, 1967).

The imogolite-like and halloysite-like structures suggested here for allophane differ from earlier structural models (see Wada, 1979) in the amount of Al^{IV} required.

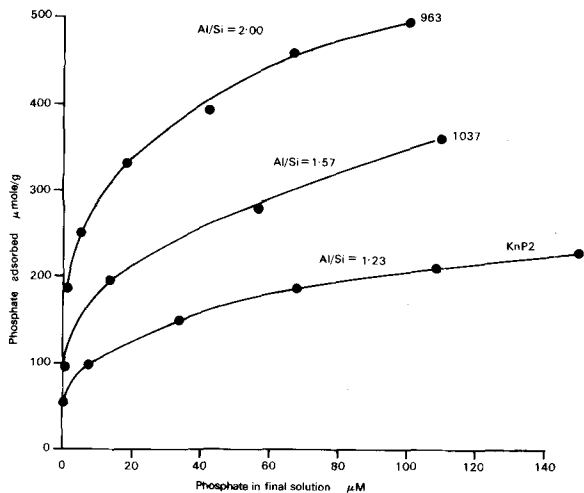


Figure 6. Phosphate adsorption isotherms (0.01 M CaCl_2 , 23°C , 16 hr, pH = 5.5–6.3).

Previous evidence for Al^{IV} comes from XRF data which are very sensitive to fluctuations in temperature; some ambiguity is involved (Wada, 1979). The present XRF and pyridine-adsorption data suggest that only a very small proportion of Al^{IV} sites are present in these allophane samples. Thus the Al is mainly in octahedral sites, and the octahedral sheet provides the structural framework for the wall of allophane spherules.

Allophanes of intermediate composition have spectral features (Figures 1–4) which suggest that they are mixtures of “proto-imogolite allophane” and KnP1 type (Al/Si = 1.0) allophane. Samples 1034 and 1035 have high $\text{H}_2\text{O}(+)/\text{Al}_2\text{O}_3$ molar ratios suggesting that many defects or pores exist where $\text{Al}(\text{OH})\text{H}_2\text{O}$ groups could occur. These data also suggest a possible alternative model for the allophane series. Such a model has “proto-imogolite” as the basic allophane structure with condensed silicate units being added to the “proto-imogolite” surface as the silica content increases. Most of the silicate units would have to be on the internal surface and bond to the isolated Si tetrahedra to explain the decrease in intensity of the 975 cm^{-1} and 348 cm^{-1} bands and the increase in intensity of the 1020 cm^{-1} band as the Al/Si ratio decreases. Such adsorbed silicate could block active AlOH sites where phosphate would otherwise adsorb and where a positive charge would develop.

Wada (1977) indicated that volcanic ash soils also contain “allophane-like” material. “Allophane-like” material is the fraction dissolved by citrate-dithionite reagent and as such it is never observed directly. It may represent the Fe-rich or Al-rich part of the allophane wall or other defects, rather than representing a separate structure.

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Резюме—Образцы, содержащие аллофан с молярными отношениями Al/Si от 1,0 до 2,0, были исследованы методами инфракрасной спектроскопии, рентгеновской флуоресценции, и фосфатной адсорбции. Инфракрасные спектры аллофана с отношениями Al/Si близкими к 2,0 показали, что оболочка аллофановых сфер состоит из имоголитовых структурных единиц похожих на «прото-имоголит». Рентгеновская флуоресценция не дала ясного доказательства присутствия Al в тетраэдрических структурах (Al^{IV}), тогда как результаты пиридиновой адсорбции указывают на то, что небольшое количество кислотных структур Бронстеда ($\text{Al}^{\text{IV}}\text{OH}$) присутствует в аллофанах богатых кремнеземом. Кислотные структуры Льюиса (AlH_2O) присутствуют как в аллофанах богатых кремнеземом, так и в аллофанах богатых алюминием. Результаты показывают, что основой для аллофановой структуры является октаэдрический лист.

Аллофаны с пропорциями Al/Si близкими к 1,0 содержат уплотненные силикатные единицы. Возможные расположения этих единиц находятся на наружной поверхности октаэдрического листа Al для галлузитообразной структуры или связаны с внутренней поверхностью имоголитообразной структуры. Аллофаны с отношениями Al/Si между 1,0 и 2,0 представляют смесь «прото-имоголитовой» структуры и аллофан (Al/Si = 1,0) структуры. [N.R.]

Resümee—Proben, die Allophan mit molaren Al/Si-Verhältnissen von 1,0 bis 2,0 enthielten, wurden mittels Infrarotspektroskopie, Röntgenfluoreszenz, und Phosphatadsorptionsmethoden untersucht. Die Infrarotspektren der Allophane mit Al/Si-Verhältnissen nahe 2,0 zeigten, daß die Wand der Allophankügelchen aus Einheiten mit Imogolitstruktur aufgebaut sind, die dem "Proto-Imogolit" ähnlich sind. Die Röntgenfluoreszenzuntersuchung brachte keinen eindeutigen Hinweis für Al auf Tetraederplätzen (Al^{IV}). Die Ergebnisse der Pyridinadsorption deuten darauf hin, daß in den Silizium-reichen Allophanen eine kleine Anzahl von Bronstedsäureplätzen ($Al^{IV}OH$) vorhanden sind. Lewissäureplätze (AlH_2O) sind sowohl in Silizium-reichen als auch in Aluminium-reichen Allophanen vorhanden. Dieses Ergebnis deutet darauf hin, daß das Gerüst der Allophanstruktur eine Aluminiumoktaederschicht ist.

Allophane mit Al/Si-Verhältnissen nahe 1,0 enthalten kondensierte Silikateinheiten. Die möglichen Lagen für diese Einheiten sind auf der äußeren Oberfläche der Aluminiumoktaederschicht, wodurch sie eine Halloysit-ähnliche Struktur ergeben, oder sie sind an die innere Oberfläche einer Imogolit-ähnlichen Struktur gebunden. Allophane mit Al/Si-Verhältnissen zwischen 1,0 und 2,0 scheinen Mischungen aus der "Proto-Imogolit"-Struktur und der Allophan ($Al/Si = 1,0$) struktur zu sein. [U.W.]

Résumé—Des échantillons contenant des proportions molaires Al/Si de 1,0 à 2,0 ont été examinés par des méthodes de spectroscopie infrarouge, de fluorescence aux rayons X, et d'adsorption de phosphate. Le spectre infrarouge de l'allophane avec des proportions Al/Si près de 2,0 montre que la paroi des sphérules d'allophane est composée d'unités structurales d'imogolite semblables à la "proto-imogolite." La fluorescence aux rayons X n'a pas démontré clairement la présence d'Al dans les sites tétraédres (Al^{IV}), tandis que les résultats d'adsorption de pyridine suggèrent qu'un petit nombre de sites acides Bronsted ($Al^{IV}OH$) sont présentes dans les allophanes riches en silice. Des sites acides Lewis (AlH_2O) sont présents à la fois dans les allophanes riches en silice et dans ceux riches en aluminium. Les résultats suggèrent que la charpente pour la structure allophane est un feuillet Al octaèdre.

Des allophanes avec des proportions Al/Si près de 1,0 contiennent des unités de silice condensées. Les positions possibles pour ces unités sont sur la surface extérieure du feuillet octaèdre Al pour donner une structure semblable à l'halloysite, ou liées à la surface intérieure d'une structure semblable à l'imogolite. Les allophanes ayant des proportions d'entre 1,0 et 2,0 semblent être des mélanges de la structure "proto-imogolite" et de la structure semblable à l'allophane ($Al/Si = 1,0$). [D.J.]