THE STRUCTURE OF "IMOGOLITE"

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ABSTRACT

The structure of "imogolite," first described in 1962, was studied with the type specimens formed by weathering of pumice and glassy volcanic ash. Chemical analyses give the formula $1.1\ SiO_2 \cdot Al_2O_3 \cdot 2.3\text{–}2.8\ H_2O$ (+) without correction for allophane as an impurity. Diffraction and electron microscopic studies suggested that "imogolite" appears in a paracrystalline state forming threads with diameter 100 to 300 Å, which consist of the chain units with the repeat distance, 8.4 Å and with the mean interchain separation, 17.7 Å. The density of the imogolite film measured by displacement with water is 2.63 to 2.70, while that measured by suspension in heavy liquids is 1.70 to 1.97. The presence of many micropores between the chain units, about 55% is estimated from the difference between the two density values and from the maximum adsorption of water vapor. The progressive change of the X-ray pattern and weight loss by heating suggests rearrangement and linking of the chain units at 50 to 250°C, and breakdown of their structure by dehydroxylation above 250°C.

"Imogolite" is structurally distinct both from allophane and from known layer or chain clay minerals. Preliminary analyses indicate a 1:2 chain structure unit for "imogolite" with the structural formula $(Al_8O_4 \cdot OH_{20} \cdot 4H_2O)_2(Si_8O_{10} \cdot OH_4)$.

INTRODUCTION

The name imogolite was first used by Yoshinaga and Aomine (1962b) for a component present in the clay fractions of the soil ("Imogo") derived from glassy volcanic ash. It was differentiated from coexisting allophane on the basis of dispersion characteristics in aqueous media (acid *vs.* alkaline dispersion), several broad yet intense X-ray diffraction bands, an endothermic peak at 410 to 430°C on the DTA curve, and its appearance as a thread of diameter 100 to 200 Å in the electron microscope. The name imogolite for a new mineral species is presently under consideration by the Commission on New Minerals and Mineral Names, IMA, which has referred it to the Committee on Nomenclature of IAPEA for advice. Inasmuch as a decision on this name will probably not be forthcoming for some time, "imogolite" is used in this paper for convenience.

A mineral component showing similar features has later been found in gel films in weathered pumice beds (Miyauchi and Aomine, 1966), in soil clays derived from volcanic ash (Aomine and Miyauchi, 1965; Kawasaki and Aomine, 1966; Yoshinaga, unpublished) and from pumiceous tuff (Jaritz, 1967). An infrared spectroscopic study (Wada, 1966) has suggested further possible differentiation of "imogolite" from allophane on

the basis of their major Si–O stretching frequencies (990 and 925 cm^{-1} vs 1010 and 945 cm^{-1}).

An understanding of the structure of "imogolite" is important not only in itself but also in relation to the structure of amorphous aluminum silicates, allophane, as its close relatives. The structure of "imogolite", however, has not been elucidated. The main difficulties are that "imogolite" shows no obvious relations to known clay mineral structures and occurs only as submicron size "crystals". An evaluation of chemical, infrared and morphological data on "imogolite" and allophane led Wada (1967) to postulate a hypothetical chain structure unit common to these two members, but no critical diffraction and density data for "imogolite" were available at that time.

Recently an electron microscopic examination of two "imogolite" specimens has revealed directly a parallel alignment of such chain units with a separation of 18 to 20 Å in the "imogolite" thread (Yoshinaga, Yotsumoto and Ibe, 1968). An electron diffraction pattern also yielded results similar to the X-ray powder pattern, but with considerable arcing of some of the reflections.

The present study extends the previous work, and provides a variety of additional data on "imogolite".

SAMPLE DESCRIPTION

Three samples of "imogolite" were studied; two are macroscopic gel films, "Ki-G" and "Ka-G" formed in the Kitakami and Kanuma pumice beds, respectively (Shioiri, 1934; Kanno, Kuwano and Honjo, 1960; Miyauchi and Aomine, 1966; Wada and Matsubara, 1968), and another is "imogolite" in a fine clay fraction (<0.2 μm) of a glassy volcanic ash soil, Lab. No. 905 (Yoshinaga and Aomine, 1962b). Preliminary alkaline dispersion of this soil removes an allophane fraction, "905-Ak," and the subsequent acid dispersion makes it possible to collect the remaining "imogolite" fraction, "905-Ac."

The gel films swelled with water appear translucent to semitranslucent. They occur exclusively covering the surface of the pumice grains or filling their interstices, but not within the pumice grains. Inclusion of small pumice grains and organic matter in the gel film is noted under the optical microscope. The mean index of refraction obtained with the air-dry material is in the range 1.47 to 1.49 (Shioiri, 1934; Kanno, Kuwano and Honjo, 1960; Miyauchi and Aomine, 1966). The gel films show in part a double refraction, but their small flakes (ca. 0.3 X 0.2 mm) always give a typical powder pattern of "imogolite," irrespective of the presence or absence of the double refraction. In relation to this, the development and stacking of a planar net structure which consists of twisting imogolite threads were revealed in the electron microscope by the carbon replica technique (Wada and Matsubara, 1968; Yoshinaga, Yotsumoto and Ibe, 1968).

In preparation, all the samples were treated first with 30 percent H_2O_2 and then, successively with $Na_2S_2O_4$-$NaHCO_3$-Na citrate and with 2 percent Na_2CO_3 (Jackson, 1956) for removal of organic matter and extractable oxides. During these treatments, pumice grains admixed in the gel films were removed as much as possible either by hand-picking or by shaking-decantation. After the treatments, the samples were washed successively with water, ethyl alcohol and acetone, and air-dried.

DIFFRACTION STUDIES

X-ray diffraction. The random and "parallel" orientation X-ray patterns were obtained by the use of a Geigerflex X-ray diffractometer. The specimen for the latter was prepared by 20 kc sonic wave dispersion of the air-dry sample in an acid medium (pH, 4.0; HCl) and allowing the dispersed clay to dry in air on a glass slide.

The major features of the X-ray pattern, which were common to the three samples examined here, are seen in Figure 1. There were some differences in the peak intensity and resolution between "Ki–G" and other two samples. The trend suggested a higher content and/or crystallinity of "imogolite" in "Ki–G".

A notable orientation is evidenced from comparison of the patterns for the random and "parallel" orientation specimens (Fig.1). The parallel
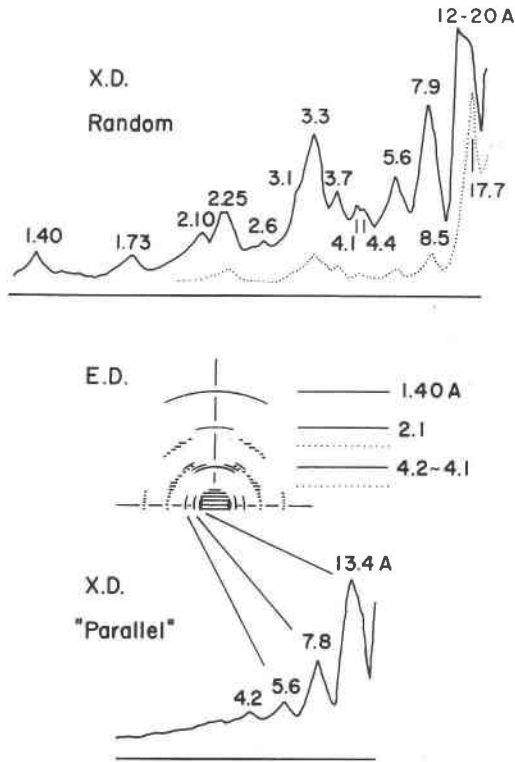

Fig. 1. Diffraction patterns of "imogolite," "Ki-G." X.D.: X-ray pattern. A dotted line shows the X-ray pattern at 300°C on one half the intensity scale. E.D.: electron diffraction pattern.

orientation enhances 12–20, 7.8–8.0 and 5.5–5.6 Å bands relative to the 3.3, 2.25 Å and other minor bands. No integral relationship such as found for ordinary layer silicates, however, is found between the *d*-values of the enhanced bands. This has constituted a puzzling aspect in the interpretation of the X-ray pattern of "imogolite" (Yoshinaga and Aomine, 1962b; Wada, 1967).

Also puzzling is the effect on the X-ray pattern of heating at 100 to 300°C (Yoshinaga and Aomine, 1962b; Aomine and Miyauchi, 1965). Re-examination of this temperature effect was carried out by X-raying the specimen on a heating stage. Particular attention was given to the quantitative aspects and reversibility of the changes. The results are shown in Figure 2, where the diffraction intensities at the low and high angle edges of the broad 12–20 Å band, and those at 7.8–8.0 Å, are plotted against temperature.

Heating at 50 to 100°C results in remarkable intensity increase at the low angle edge of the 12–20 Å band, together with a slight but significant shift of the edge to the high angle side (Fig. 2). Concurrently, the 4.1 and 3.7 Å bands, particularly the former, became sharper and enhanced, while the broad 3.3 Å band showed a considerable intensity decrease. The corresponding weight loss, shown also in Figure 2, suggests that this change associates with removal of adsorbed water. The latter was confirmed from
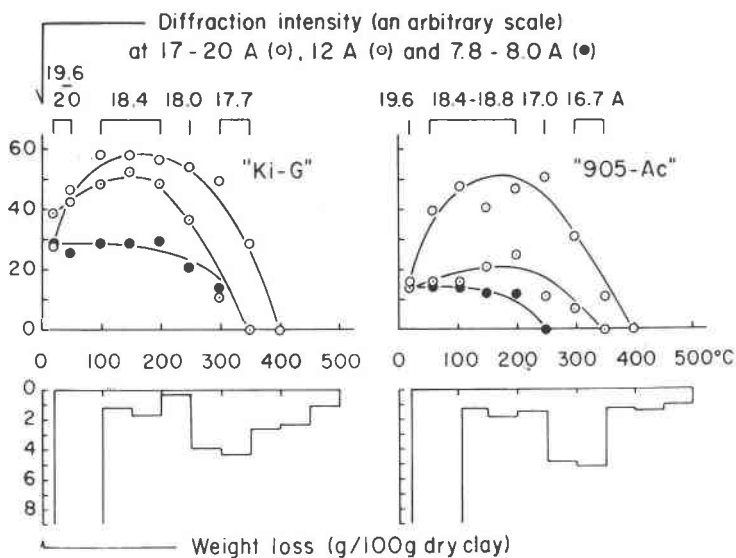

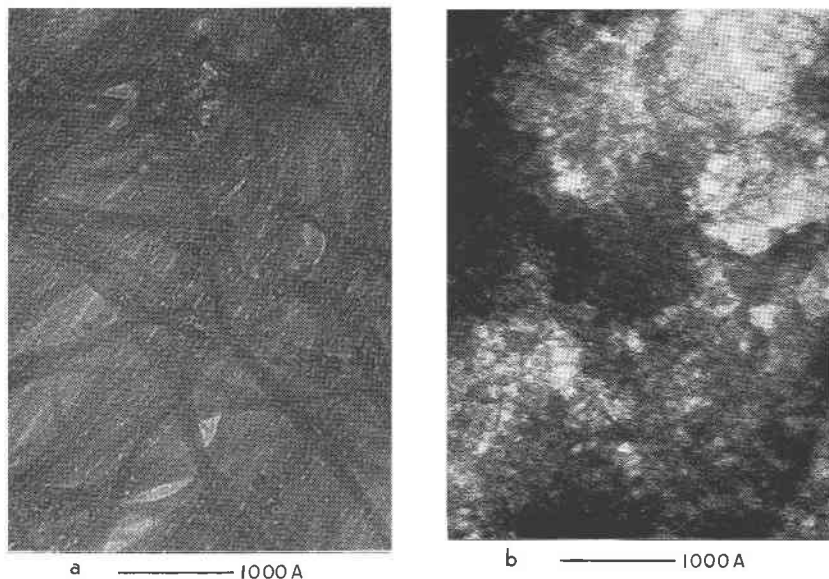Fig. 2. Effects of heating on the X-ray pattern and weight loss of "imogolite," "Ki-G" and "905-Ac."

FIG. 3. Electron micrographs of "imogolite," "Ki-G" (a) and allophane, "905-Ak" (b).

an X-ray analysis of the specimen over P_2O_5 in vacuo in the sealed enclosure, where the same change as that described above took place at room temperature.

The second change occurs by raising the temperature from 200 to 250° C ("905-Ac" and "Ka-G") or 300°C ("Ki-G") (Fig.2). The broad 12–20 Å band now apparently merges into a fairly sharp peak at 17.0 to 17.7 Å (Fig. 1, X.D., random; dotted line). A transitional second order reflection, though broad and very weak, appears at 8.0 to 8.5 Å. All the other peaks and bands become much weaker and broader, and the change becomes almost irreversible. Finally, dehydroxylation takes place above 250°C and results in destruction of the imogolite structure at 350 to 400°C. The weight loss suggests that about 65 to 75 percent of the total structural OH groups are lost between 250 and 500°C.

Electron microscopy and diffraction. Electron micrographs and diffraction patterns were obtained with the specimens dispersed with 400 kHz ultrasonic waves. A droplet of the suspension was dried in air on a microgrid and examined at 80 or 100 kV using a JEM-7A electron microscope with an anti-contamination device. Gold was used as a standard substance for calibration of *d*.

Nearly parallel alignments of the "imogolite" chain units with a separation of 18 to 20 Å are seen in Figure 3a. Estimation of the width of the

chain unit itself was more difficult, but that of the relatively dense core was estimated 10 to 12 Å at higher magnifications. Besides the chain units, peculiar ringlets and their aggregates are often seen in the micrographs, but neither their identity nor their relationship to "imogolite" is as yet clear.

The thick bundles of the chain units were selected for diffraction study. The resulting pattern is reproduced in Figure 4 and also given in a schematic way in Figure 1 to show details which are difficultly seen in the print. The pattern as a whole has the appearance of a rotation diagram. Considerable arcing occurs, however, along the powder lines due to incomplete orientation of the chain units.

The three sharp diffraction arcs appear at 4.1–4.2, 2.1 and 1.40 Å on the meridian which is parallel to the direction of elongation of the chain units (Fig. 4). Relative enhancement of these reflections by parallel chain orientation is evident in comparison with the X-ray patterns (Fig. 1). Three broad diffraction arcs appear on the equator, which correspond to those enhanced on the X-ray pattern by 'parallel' orientation.

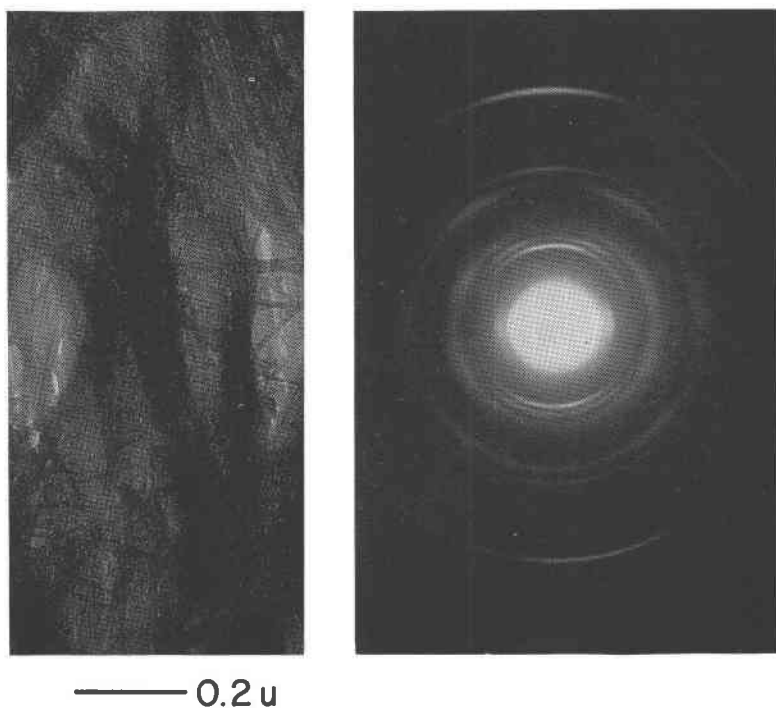Aside from the two major directions, appear several diffraction arcs

0.2 u

FIG. 4. Electron diffraction pattern of "imogolite," "Ki-G," selected area.
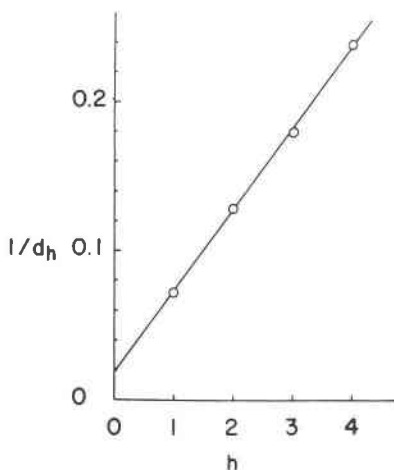
FIG. 5. Plot of $(1/d_h)$ for equatorial reflections of "imogolite," "Ki-G" against their order, h.

and rings (Figs. 1 and 4), which are seen only on the X-ray pattern for the specimen in random orientation. Fairly sharp arcs with the spacings 3.7 and 3.1 Å appear apparently forming the second layer line, together with the strong 4.1–4.2 Å arc on the meridian. The two strong but broad bands with maxima at 3.3 and 2.25 Å on the X-ray pattern are still diffuse and weaker on the electron diffraction pattern. These show, however, discernible intensity maxima on the probable first- and third-layer lines, respectively.

The finer morphology and electron diffraction of allophane may arouse interest here, since allophane has often some fibrous morphology (Yoshinaga and Aomine, 1962a; Aomine and Wada, 1962; Wada and Matsubara, 1968) and chemical composition close to that of "imogolite" (Fig. 6). As a sample of allophane close to imogolite, "905-Ak" was examined in the present study. On the X-ray pattern, it almost lacks three strong "imogolite" bands at 12–20, 7.8–8.0 and 5.5–5.6 Å. Two bands with maxima at 3.3 and 2.25 Å are seen but these are broader and less intense than those for "905-Ac" (Yoshinaga and Aomine, 1962a).

The morphological difference between this allophane and imogolite is evident from comparison between Figures 3a and 3b. Generally allophane shows a fine granular texture, but close examination reveals presence of entangled fibrils somewhat similar to the chain unit of imogolite, that may suggest possible morphological and structural transitions from allophane to imogolite. No well-defined alignment of these fibrils is seen, and the selected area electron diffraction gives only a broad ring pattern corresponding to the powder X-ray pattern of allophane.
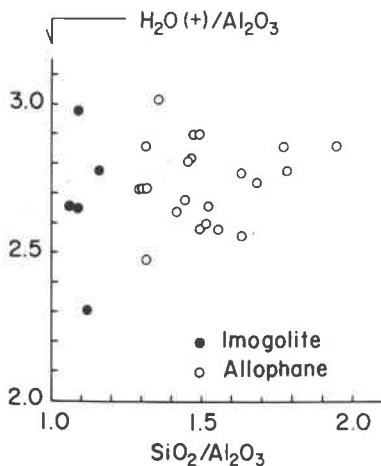
FIG. 6. The SiO_2/Al_2O_3 and $H_2O(+)/Al_2O_3$ ratios for "imogolite" and allophane. See Table 1, and Yoshinaga (1966).

Interpretation of diffraction data. The results of electron microscopy and diffraction studies indicate the presence of a unique chain unit for imogolite. If the chain axis of imogolite is denoted by b, the separation of the layer lines (Fig. 1) indicates that the b-axis has a repeat distance of 8.4 Å. From the observed orientation of the chain units (Figs. 3a and 4), it is expected that the equatorial electron diffraction arcs or the equivalent X-ray bands arise from some stacking of the nearly parallel chain units. Actually the observed d-value can neither be explained by a simple layer lattice nor by a two-dimensional (hl) lattice.

A similar situation is found for assemblies of biological chain molecules, such as collagen, DNA and so on (Vainshtein, 1966). Complete statistical rotation and continuous shifts are characteristic of those chain assemblies. The theoretical treatment of their equatorial reflections (Guinier, 1963; Vainshtein, 1966) predicts a relationship

$$(1/d_h) = (h + \epsilon)/\bar{a}$$

where $(1/d_h)$ is the reciprocal of the d-value measured on the hth equatorial reflections, a is the statistical mean distance between the chain units, and ϵ is a constant depending on the regularity of the chain-unit arrangement. As a good approximation, ϵ takes a value of $\frac{1}{8}$ for any set of parallel packing of the chain units, where their intersections with a plane normal to the axis of the chain unit would form either a plane lattice or the two-dimensional equivalent of a paracrystal. The ϵ increases up to $\frac{1}{4}$ for the paracrystalline assemblies of the chain units in which their

parallel packing is not assured. The paracrystalline states here refer to those in which the distribution of the nearest chain units is reasonably distinct and described by a, but the more distant the neighbor, the more diffuse becomes the distribution.

Then, the linearity of the plot of the $(1/d_h)$ measured on the X-ray pattern (Fig. 1, X.D., 'parallel') against the h (Fig. 5) may serve to indicate that the diffraction is governed by such arrangement of the chain units. The appearance of the well-pronounced band maxima suggests/the presence of the pore space between the chain units (Vainshtein, 1966). The a calculated by applying $\frac{1}{8}$ and $\frac{1}{4}$ for the ϵ is 15.8 to 17.5 Å and 17.5 to 17.9 Å, respectively. The relative constancy of the latter suggests that considerable deviation from the parallel packing of the chain units occurs in the "imogolite" thread in the air-dry state. Formation of "imogolite" paracrystal may well be expected from its occurrence as gel films containing much water, which causes the chain units to be in incomplete contact.

All the changes associated with heating or evacuation may now be interpreted in terms of the changes in the arrangement of the chain units. The change at 50 to 200°C (Fig. 2) suggests improvement of parallel alignment of the chain units by removal of interstitial water, and then, by thermal motion of the atoms constituting the chain. The particular intensity increase at the low-angle edge in the broad 12 to 20 Å band suggests elliptical but not circular cross section of the chain units and their contact at edges along their major axis. At 250 to 300°C, the neighboring chain units may link to each other side by side with the mean separation 17.0 to 17.7 Å, which results in development of very thin sheets of "imogolite" along random directions. Then, the reaction would no longer be reversible. The thin sheet formation is inferred from comparison of the X-ray pattern (Fig. 1, X.D., random; dotted line) with that derived for an ideal one-dimensional paracrystal (Guinier, 1963; Vainshtein, 1966).

On the basis of the rectangular (hk) lattice with $a = 17.7$ Å and $b = 8.4$ Å, the three meridian arcs on the electron diffraction pattern (Fig. 1) can be indexed as 02, 04 and 06, and the three arcs with $d = 4.1$ 3.7 and 3.1 Å on the second layer line as 12, 22 and 42. Several diffraction bands with maxima at 4.4–4.0, 3.3, 2.55, 2.25 and 1.7 Å remain unexplained by interference between the chain units. Generally, their relative intensities decreased with increasing chain orientation either on the X-ray or electron diffraction pattern. It suggests that these probably arise from interatomic interference within a chain unit. Similar bands, though less intense and broader, appear on the X-ray pattern of allophane (Yoshinaga and Aomine, 1962a).

CHEMICAL ANALYSES

Elemental analysis. The oxide formulas derived from elemental analyses of "imogolite" are listed in Table 1. From most samples, the extractable oxides were removed by treatments with $Na_2S_2O_4$-$NaHCO_3$-Na citrate and 2 percent Na_2CO_3 (Jackson, 1956). The sum of SiO_2, Al_2O_3 and H_2O (+) constituted 96 to 98 percent of total analysed material. The oxides of alkali or alkaline earth metal as an exchangeable cation constituted additional 0.7 to 1.7 percent, which was counted in the oxide formula as H_2O (+) by conversion. The content of other elements was insignificantly small and variable.

TABLE 1. CHEMICAL ANALYSES DATA FOR "IMOGOLITE"

Sample	Empirical formula $SiO_2:Al_2O_3:H_2O(+)$	$(Me^+)/Al$[a]	Reference
"Ki-G" (i)	1.09:1.00:2.31	0.046	—
(ii)[b]	1.11:1.00:2.65	0.028	—
"Ka-G"[b]	1.09:1.00:2.98	0.093	Miyauchi and Aomine (1966)
"Im-G"[c]	1.16:1.00:2.78	0.026	Yoshinaga (unpublished)
"905-Ac"	1.06:1.00:2.66	0.031	Yoshinaga and Aomine (1962b)

[a] Atomic ratio of exchangeable cation (Me^+) to Al.

[b] Sample without 2% Na_2CO_3 treatment.

[c] Gel film in Imaichi pumice bed.

All the samples are not pure "imogolite." Admixing of small amounts of allophane and/or fine pumice grains is expected from their occurrence (Yoshinaga and Aomine, 1962a, b; Wada and Matsubara, 1968) and methods of preparation. The difference in the chemical composition between "imogolite" and allophane can be seen in Figure 6, where a boundary may be drawn at the SiO_2/Al_2O_3 ratio 1.1–1.2. The SiO_2/Al_2O_3 ratio for all the "imogolite" samples exceeds slightly an ideal ratio 1.0. Whether or to what extent this slight excess of Si is essential or due to admixture from allophane, cannot yet be decided.

The $H_2O(+)/Al_2O_3$ ratio shows more variation and no definite difference between "imogolite" and allophane (Fig. 6). For "Ki-G" a significant amount of $H_2O(-)$, up to 2 percent on the oven-dry basis, remained unremoved by heating at 105°C, whereas it was removed by evacuation

over P_2O_5 at 25 to 30°C. The overestimation of $H_2O(+)$ due to this unremoved $H_2O(-)$ is corrected in the formula given for "Ki-G" and "Im-G" in Table 1.

Adsorption of water vapor. The predominance of Al in the 'imogolite' composition suggests importance of distinction between water coordinated to Al and that adsorbed on the chain-unit surface. The adsorption of water vapor at various relative pressures was determined by gravimetry after equilibration of the sample with an atmosphere over an appropriate concentration of sulfuric acid at 25 to 30°C. The reference sample weight was obtained by drying over P_2O_5 in vacuo.

The adsorption and desorption curves of water vapor by "Ki-G" and "905-Ac" are shown in Figure 7, where the desorption curves obtained by Mooney, Keenan and Wood (1952) for Ca- and Na-montmorillonites are also shown for comparison. The curve for "Ka-G" was found to run between the "Ki-G" and "905-Ac" curves. "Imogolite" shows a marked adsorption of water and its magnitude is greater even than that of montmorillonite. This is expected from the presence of the separate chain units in the "imogolite" thread, which can provide large specific
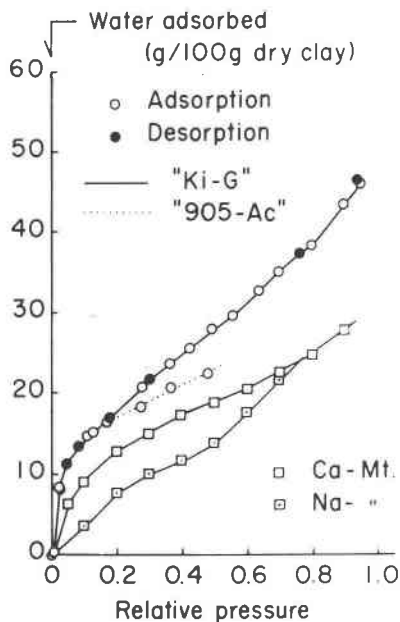

FIG. 7. Adsorption of water vapor by "imogolite," "Ki-G" and "905-Ac" at 25 to 30°C, and Ca- and Na-montmorillonites at 20°C (Mooney, Keenan and Wood, 1952).

surface area. The effect of exchangeable cation, in this case Na, may be minor in view of its small content (24 to 42 me¬/100 g dry clay). No detectable hysteresis loop appears on the adsorption and desorption curves for "Ki-G". The results suggest the presence of many micropores which have a fairly uniform size and can accommodate up to about 50% of water on the dry-weight basis.

In the range of relative pressure 0.2 to 0.05, "imogolite" shows a tendency to retain some water more strongly than does either Ca- or Na-montmorillonite (Fig. 7). This water may be assigned tentatively to that in coordination with Al in the chain unit. An approximate estimate of its amount is obtained by extrapolation of the nearly linear portion of the adsorption curve to zero relative pressure. This gives a $H_2O(co)/Al_2O_3$ ratio 1.18, where (co) stands for coordination with Al.

In conclusion, the best empirical formula for "imogolite" may be expressed as follows; $1.1 SiO_2 \cdot Al_2O_3 \cdot 2.3\text{-}2.8H_2O(+) \cdot 1.2H_2O(co)$.

Density Determination

The density of the "imogolite" samples was determined in two procedures. The first is an ordinary pycnometer method using water as the displacement liquid. The second is a float-sink test of the "Ki-G" film in an appropriate heavy liquid. For the latter, the gel films were first swelled with water, and then, washed progressively with organic solvents in the order: methanol, acetone, benzene, and carbon tetrachloride. After completion of the washing with each solvent, two to three flakes of the gel film were placed in a small amount of the same solvent. The float-sink test was made by incremental addition of acetylene tetrabromide $C_2H_2Br_4$. The density of the gel film was narrowed down to the interval between two test liquids. In both the determination procedures, entrapped air was removed by suction with an aspirator in a sealed enclosure.

The density of "imogolite" determined by displacement with water is shown in Table 2. There seems to be a broad correlation between crystallinity and density of the sample. Much lower values, 1.98 to 2.30 were reported by Birrell and Fieldes (1952) for soil allophane with the $SiO_2/Al_2O_3 = 1.2$ to 2.4. The values for "Ki–G" and "Ka–G" are comparable with or even greater than those quoted for kaolinite, 2.60 to 2.68 (Grim, 1953). Even the smallest value for "905-Ac" exceeds 2.32 to 2.35 given by Aomine and Yoshinaga (1953) for the coarse volcanic glass fragments separated from a similar volcanic ash soil.

The density of a clay determined by displacement with water would be higher than its true value, if there is adsorption of water on the surface of the clay, and if this water has higher density than normal water. Much

TABLE 2. DENSITY AND PORE SPACE DATA FOR "IMOGOLITE"

Sample	Procedure	Density	Pore Space %
"Ki-G"	I; H_2O[a])	2.70 ± 0.05[c]	
"Ka-G"	I; H_2O[a])	2.63 ± 0.03[d]	
"905-Ac"	I; H_2O[a])	2.53 ± 0.03[d]	
"Ki-G"	II; CH_3OH $-C_2H_2Br_4$[b])	1.70 ± 0.03	51.4
"Ki-G"	II; $CH_3COCH_3-C_2H_2Br_4$[b])	1.81 ± 0.03	46.5
"Ki-G"	II; C_6H_6 $-C_2H_2Br_4$[b])	1.95 ± 0.02	40.0
"Ki-G"	II; CCl_4 $-C_2H_2Br_4$[b])	1.97 ± 0.02	71.4

[a] Pycnometer method; displacement liquid.

[b] Float-sink test; heavy liquid composition.

[c] Density expressed for the material dried over P_2O_5 in vacuo.

[d] Density expressed for the oven-dry material (105°C).

lower values obtained from the float-sink test in the heavy liquid (Table 2) may at first sight suggest this possibility. Calculation showed, however, that density of "imogolite" as low as 1.70 could occur only when all the adsorbed water (*e.g.*, 50% on the oven-dry basis) has an unlikely high density such as 1.83. For montmorillonites, Low (1961) concluded from his critical review on many related data that the density of adsorbed water is slightly lower than that of normal water (2 to 3% at its minimum). An interpretation along the same line would also fail to explain the observed variation for different heavy liquids.

Alternatively, all the results can be interpreted in terms of the presence of micropores which can accommodate water and other small solvent molecules, but not the larger $C_2H_2Br_4$ molecule. The presence of such micropores has already been suggested from the preceding studies. Then, the higher density obtained by displacement with water may be taken as an indication of dense packing of atoms in the chain unit, and hence, crystallinity of "imogolite".

According to the latter view, the difference between the density values (Table 2) would give a measure of such pore space in the gel film. Calculation was made by assuming filling of the micropores with each solvent of normal density and their complete exclusion of $C_2H_2Br_4$. The calculated pore space is in the range 40 to 50 percent for CH_3OH, CH_3COCH_3 and C_6H_6, whereas a much higher value is obtained for CCl_4 (Table 2). The van der Waals thickness of the former three molecules is in the range 3.4 to 4.0 Å, while the equivalent diameter of the latter CCl_4 amounts to 7.1 Å. The differences in the molecular size and shape suggest that the abnormally high CCl_4 value resulted from its exclusion from the micropores,

where C_6H_6 probably remained from the preceding washing. Then, the assumed exclusion of the $C_2H_2Br_4$ molecule may also be justified, if it is regarded as a cylindrical rod of diameter 6.5 Å.

A curvilinear relationship is found between the calculated pore space for the respective solvent and its molar volume (Fig. 8). If this relationship holds for smaller molecules, the pore space for water is estimated close to 55 percent. On the other hand, the maximum water adsorption in Fig. 7 (ca. 46 g H_2O/100 g dry clay) and the density of the chain unit (2.66) give also the pore space 55.0 percent. The latter calculation naturally includes less certain assumptions such as filling up of all the pore with water, but the agreement between the two estimates may be taken
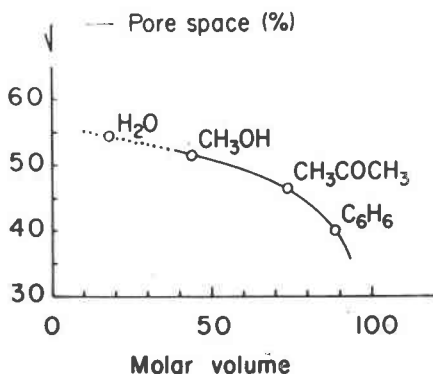

FIG. 8. Relationship between the pore space of "imogolite," "Ki-G" measured by immersion in various solvents and their molar volume.

as an indication of the limited expansion of the interchain separation even in water. Then, the interchain pore space of "imogolite" in the air-dry state is also estimated close to 55 percent.

THE STRUCTURE OF "IMOGOLITE"

Packing of chains. From the evidences brought together in the foregoing sections, it is concluded that "imogolite" is structurally distinct both from allophane, and from known layer or chain clay minerals, and has its own unique chain unit. The low degree of order in the packing of the chain units and their hydration, however, do not permit direct deduction of the size of the "naked" structural unit except for the unit length along the chain axis. In order to estimate its approximate size, we now assume as a first approximation a cylindrical structure unit for "imogolite." The diffraction data show that the unit length of the cylinder is 8.40 Å. The volume, and hence, the diameter (D) of the cylinder containing m empirical formula weights can be calculated from the simplified for-

mula $SiO_2 \cdot Al_2O_3 \cdot 2.5H_2O$ and the density of the chain unit, 2.66. Then, the interchain pore space is also calculated for a parallel assembly of the respective cylindrical rods with the separation of 17.7 Å by assuming 6-fold coordination, which is usually retained in the assembly of chain molecules (Vainshtein, 1966). Comparison of the calculated and observed interchain pore space serves to determine the probable m per structure unit of "imogolite" (Fig. 9). The plot indicates that $m = 8$ is most likely, but $m = 7$ and 9 cannot be ruled out completely in view of approximations involved in both experimental determination and deduction. The D, 12.5 Å calculated for the structure unit with $m = 8$, also is not unreasonable in comparison with $D < 17.7$ Å derived from the diffraction data and $D \geq 10$ to 12 Å estimated on the electron micrographs.
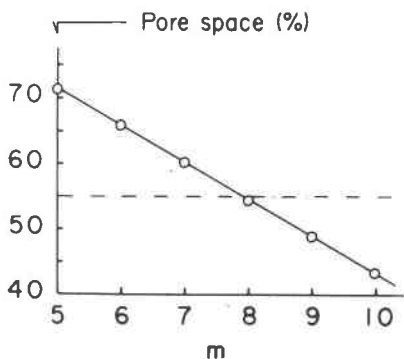

FIG. 9. The interchain pore space calculated for "imogolite" containing m formula weights per structure unit. A horizontal line shows an empirical estimate.

Structure of the chains. Beyond this point, the determination of the internal structure of "imogolite" can be advanced only by guess. Wada (1967) proposed a hypothetical chain structure unit of "imogolite" with an ideal composition $SiO_2 \cdot Al_2O_3 \cdot 2H_2O$. There are two chains consisting of AlOH octahedra, which share an edge with a neighboring octahedron on either side. The chains are linked sideways by tetrahedrally coordinated Si. The resulting composite chain would have a repeat distance 2.80 Å along its chain axis. The new evidence obtained here, particularly the chain repeat distance 8.40 Å, make this structure model unacceptable. Therefore, we must start over with an alternative guess on the basis of the amplified data in consideration of rules of general crystal chemistry.

In placing the respective atoms in the structure unit, it was assumed at first that Si and Al coordinate with 4 and 6 oxygens or hydroxyls, respectively. The latter allocation of coordination number 6 for all Al in

"imogolite" may be questioned, but is permissible in view of the small amount of exchangeable alkali cations present, which are required for the stabilization of the 4-fold coordination of Al (Iler, 1955). The atomic ratio of the alkali cation to Al in the analysed material is in the range 0.026 to 0.046 except for the one with 0.093 (Table 1). It is likely that even this small amount of exchangeable cation is retained through other mechanisms such as dissociation of the Si-OH groups.

The dominating presence of Al and H in "imogolite" and the observed 8.40 Å repeat distance along its chain axis b, suggest an important role of a hexa-aluminohydroxyl group (Fig. 10; I) in the resultant structure. The corresponding parameter for the similar octahedral layer is 8.64 Å in gibbsite and 8.95 Å in kaolinite and dickite, although for the latter two minerals, b is expanded by association with a silica sheet.

The observed extinction of either $0k$ or hk when k is odd suggests a linking of the hexa-aluminohydroxyl groups in a chain with glides along the chain axis with the component $b/2$. The zigzag linking in a plane (Fig. 10; II) or vertical stacking of either single straight (Fig. 10; III) or zigzag (Fig. 11) chain units can fulfill the above requirement. According to the above line, we can draw linking diagrams only for the structure unit with $m=8$, as illustrated in Figure 11 (I or II) but not for those with $m=7$ and 9, which therefore may be discarded at this stage.

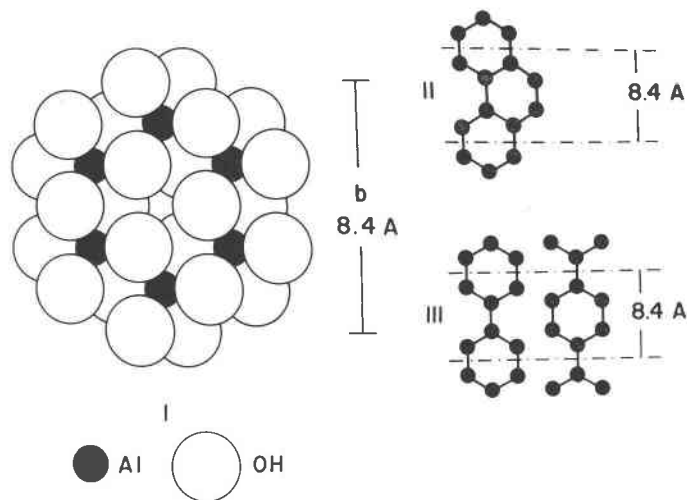The tetrahedrally coordinated Si may also form a chain or chains so as

FIG. 10. A hexa-aluminohydroxyl group (I), its zigzag linking (II) and vertical stacking of its single straight chains (III). with glides with component $b/2$. In III, the chains are displaced because they would otherwise be superimposed.
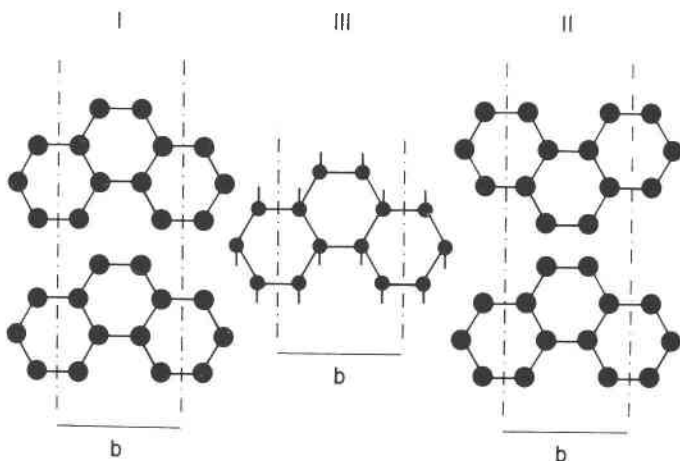
Fig. 11. Possible stacking diagrams of octahedral AlO, OH chains (I or II) and trigonal SiO chains (III) for the structure unit of "imogolite" with $m = 8$. The SiO chains (III) are supposed to intervene between the superimposed AlO, OH octahedral chains (I or II). Large and small black circles show the positions of Al and Si atoms, respectively. The positions of O atoms and OH groups are omitted. The vertical lines directed from the Si atoms above and below indicate that they locate above and below the common oxygen sheet of the trigonal SiO chains, respectively.

to confer a stability on the composite chain unit of "imogolite." An infrared spectroscopic study of imogolite in combination with deuteration Wada, 1966) indicated that practically all the OH groups, most of which likely coordinate to Al, are exposed at surface. Then, the SiO chain must intervene and have a role to connect the upper and lower AlO,OH octahedral chains.

The number of Si in the unit with $m = 8$ is fixed at 8, and the $0k$ and hk extinctions when k is odd, impose for its distribution the minimum disturbance on the symmetry set by the distribution of the Al atoms. A permissible configuration is then an hexagonal chain arrangement consisting of two trigonal SiO chains (Fig. 11; III). The Si atoms may locate either above or below the common oxygen sheet, and their vertical linking with the upper and lower AlOH octahedral chains is achieved by sharing of oxygens with the two Al atoms in the respective octahedral chains.

The placement of the Si atoms relative to the common oxygen sheet, and the placement of the resulting SiO chains relative to their upper and lower AlO,OH chains could be made in several ways, but the final configuration was determined by taking into consideration the following requirements; 1) to give conformity with the number of structural OH groups and Al-coordinated water molecules per structure unit, 2) to expose the structural OH groups as many as possible at the surface, 3) to

set the maximum width of the structure unit including the Al-coordinated water molecules close to the observed interchain separation, 17 to 20 Å, and 4) to account for the changes appeared on the X-ray pattern upon heating by rearrangement and linking of the resultant chain units.

A probable placement of the Si atoms in the SiO chains is illustrated in Figure 11; III. Then, the atomic disposition and cross-section of the whole structure unit may be depicted as shown in Figure 12. The chemical formula and the density of "imogolite" are calculated on the basis of the derived structure unit, and both show a reasonable agreement with the corresponding analytical results:

Chemical formula $SiO_2:Al_2O_3:H_2O(+)$ $:H_2O(co)$
          Calculated: 8.0 :8.0 :22.0   :8.0
          Analyzed: 8.8 :8.0 :18.4 to 22.4:9.6

Density
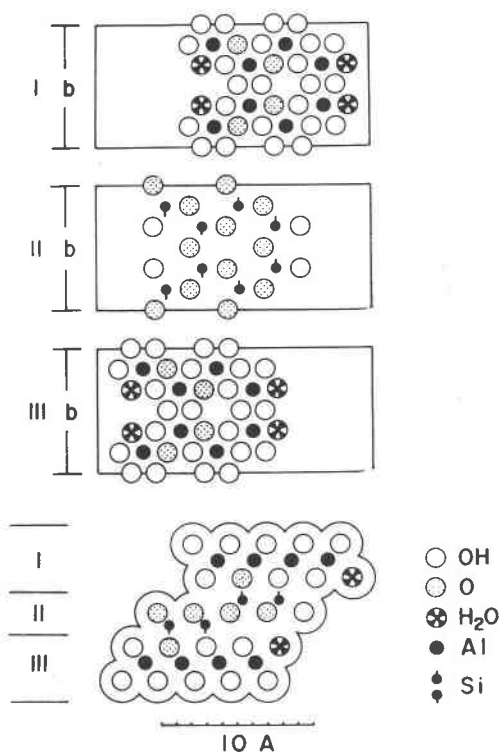   Calculated: 2.70
          Measured: 2.63–2.70.

FIG. 12. A structure unit of "imogolite" with the structural formula $(Al_8O_4 \cdot OH_{20} \cdot 4H_2O)_2$-$(Si_8O_{10} \cdot OH_4)$ and with the chain axis b.

The shortness of $H_2O(+)$ and the compensating excess of SiO_2 in the analysis may be interpreted in terms of admixing of allophane with a higher SiO_2/Al_2O_3 ratio, but may have a significance in relation to the observed limit in expansion of the interchain space. It may be expected that the siloxane chain serves in linking between the neighboring chain units.

The calculated $0k$ intensities also show a good agreement with those observed on the electron diffraction pattern (Table 3). All the structural OH groups are not exposed at surface, but the small ratio of the unexposed to the total structural OH groups 2/44 may be permissible.

The maximum and minimum widths of the "hydrated" chain unit, 20.0 and 13.2 Å are reasonable to give the observed equatorial or equiva-

TABLE 3. SPACINGS AND INTENSITIES CALCULATED AND OBSERVED FOR 0k
REFLECTIONS FROM "IMOGOLITE"

Order	d Å	$F^2 \times 10^{-4}$	$F^2 \times 10^{-8}/\sin^2\theta$ ($\lambda = 0.042$ Å)	$I_{obs.}$
1	8.40	0	0	Absent
2	4.20	650	2600	Very strong
3	2.80	5	9	Absent
4	2.10	147	147	Weak
5	1.68	0	0	Absent
6	1.40	1395	628	Medium

lent X-ray reflections (Fig. 1). The changes of the X-ray pattern associated with the step-wise heating (Fig. 2) are explained in terms of the increasing possibility of contact between the "dehydrated" chain units, and of their subsequent linking by sharing of some edge OH groups. In an ideal case, the latter would result in a sheet of the chain units with an interchain separation of 17.2 Å (Fig. 13) which accords with the spacings 17.0 to 17.7 Å observed at 250 to 300°C.

Details of bonding. The derived internal structure is inevitably of preliminary nature, since its derivation depends on many implications rather than on critical diffraction data, which are still lacking. No direct means is available to check the bonding features hereby derived, but there is at least no incompatibility between the derived structure and the known structure-dependent characteristics of "imogolite." The latter have been described in previous sections, and in a previous paper (Wada, 1967).
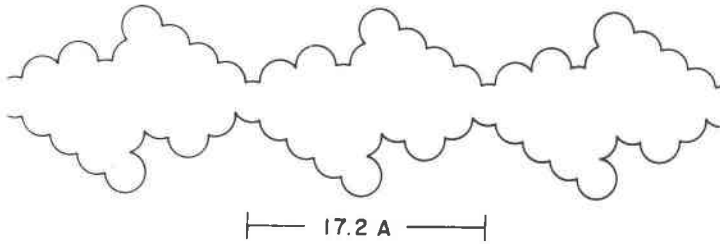
FIG. 13. The cross-section of the chain units of "imogolite" linked sideways by sharing of the edge OH groups.

Among them, only two observations in DTA and infrared spectroscopy are repeated here, because these may carry implications for two unusual bonding features in the derived structure.

The first is a partial linking between the AlOH and SiO chains illustrated in Figure 12. The number of the sharing oxygens to that of the Al atoms per structure unit is 8/16 in the derived structure of "imogolite," whereas the same ratio is 4/4 in kaolinite. This "half" linking picture is not unreasonable in view of the partial stabilization of the Al–OH groups suggested from DTA. Dehydroxylation of "imogolite" gives a small yet prominent endothermic peak at 410–430°C (Yoshinaga and Aomine, 1962b). This dehydroxylation temperature is midway between that quoted for gibbsite, 320–330°C and that for kaolinite, 575–620°C (Mackenzie, 1957).

The second feature is the large rotation of the SiO tetrahedra from an "ideal" hexagonal symmetry in the derived structure (Fig. 12). The rotation angle calculated from a formula proposed by Radoslovich and Norrish (1962) amounts to 22° in "imogolite", while that for kaolinite is in the range 9 to 11°. A relationship between this rotation of the tetrahedra and the frequencies of the major Si–O stretching absorption band was inferred by Farmer and Russell (1964). They interpreted the observed difference in the major Si–O stretching frequencies between margarite (926 cm^{-1}) and amesite (1000–990 cm^{-1})—both these minerals have high Al for Si substitution—in terms of the difference in the degree of rotation of the tetrahedra, about 21° in margarite and 11.5° in amesite. It is noteworthy that the infrared spectra of "imogolite" show two major Si–O stretching absorption maxima at 990 and 925 cm^{-1} (Wada, 1966), which are distinctly lower than those for kaolin minerals, 1120–1110 and 1040–1010 cm^{-1}, respectively. In addition to the rotation of the tetrahedra, their tilting also may serve to reduce the longitudinal dimension of the tetrahedral chains, but this is not shown in Figure 12 taking into consideration the preliminary nature of the derived structure.

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