Clays and Clay Minerals, Vol. 35, No. 5, 379–384, 1987.

IMOGOLITE SYNTHESIS AT 25°C

SHIN-ICHIRO WADA

Department of Agricultural Chemistry, Kyushu University 46
Fukuoka 812, Japan

Abstract—Imogolite was synthesized at 25°C by aging partially neutralized solutions containing monomeric silicic acid and polymeric hydroxy-aluminum ions for 7 years. Solutions having an initial Si/Al molar ratio of about 0.5 and pHs of 4.0–4.5 produced the largest yields of imogolite, followed by those having an initial Si/Al ratio of about 1, although imogolite was not the principal product. Electron microscopic examination showed a small amount of imogolite fibers embedded in a noncrystalline gel-like substance. Traces of imogolite were detected in solutions having an initial Si/Al ratio of about 2, but no imogolite was found by electron microscopy in products from solutions having an initial Si/Al ratio of about 4. Only gibbsite formed from solutions having initial Si/Al ratios of <0.27. The diameter of the tubular structural unit of the imogolite produced in these experiments was 23 ± 2Å, close to that of natural imogolite.

Key Words—Fiber, Imogolite, Infrared spectroscopy, Synthesis, Transmission electron microscopy.

INTRODUCTION

Imogolite is an aluminosilicate that consists of a tubular structural unit having an external diameter of about 20 Å. It is common in the clay fraction of soils derived from volcanic ejecta, but it has also been found in many podzols, a basalt saprolite, and a shattered sandstone (see Tait *et al.*, 1978; Wada *et al.*, 1972; Yoshinaga *et al.*, 1984; respectively).

Synthesis is one of the most direct means of understanding the mechanisms and conditions of formation of natural imogolite. Farmer *et al.* (1977) first synthesized imogolite, and Farmer and Fraser (1978), Wada *et al.* (1979), and Inoue and Huang (1985) studied the effect of pH, the Si/Al molar ratio of starting solutions, and the presence or absence of co-ions on the formation of this material. Farmer *et al.* (1979) measured the free energy and heat of formation of the synthetic imogolite. On the basis of the experimental evidence reported by these authors, the conditions under which imogolite forms in nature should be definable. It must be remembered, however, that all syntheses to date were made at ≥100°C and that the synthetic imogolite products were not identical to the natural materials, i.e., the diameter of the structural unit of the synthetic product was significantly larger than that of the natural imogolite. For this reason, additional research on the synthesis of imogolite at lower temperature appears to be needed.

Wada and Wada (1980) aged dilute solutions of hydroxy-aluminum ions and monomeric silicic acid having different Si/Al molar ratios and pHs for 100 days. They identified cationic compounds which yielded infrared (IR) spectra similar to but not as well developed as those of imogolite. In the present study, similar solutions were aged for 7 years; the formation of imogolite was confirmed by electron microscopy.

EXPERIMENTAL METHODS

Syntheses

Solutions containing monomeric silicic acid and $AlCl_3$ to Si/Al molar ratios (hereafter called Si/Al ratio) of 0, 0.266, 0.531, 1.04, 2.18, and 4.24 were prepared. The Al concentration in all starting solutions was 0.48 mM. To 400-ml portions of these solutions, 0.1 M NaOH was added to give NaOH/Al molar ratios (hereafter called NaOH/Al ratio) of 1.00, 2.00, 2.50, and 2.75. The method of preparation was essentially the same as that described by Wada and Wada (1980) except that the distilled water used to dilute the reagents was boiled for 15–20 min to sterilize it. The reagents used were of guaranteed grade from Katayama Chemical Industries Co., Japan. The resulting solutions were transferred into sterilized polypropylene bottles having fitted stoppers and aged at 25°C in the dark. During the preparation of the solutions, special care was taken to avoid contamination with microorganisms because their metabolic products, such as organic acids, can seriously affect the stability of imogolite and related substances (Inoue and Huang, 1985).

At two- or three-month intervals, a drop of the solution was taken from the bottles with a sterilized platinum wire, dried on a microgrid, and examined in an electron microscope. The solutions were aged for a period of 7 years, from August 1978 to October 1985.

Analyses

In October 1985, imogolite was identified in some of the solutions and the aging was stopped. The pH and monomeric aluminum ion concentration were determined on aliquots taken from the bottles, the latter by the 8-quinolinolate extraction method described by Wada (1986). The remainder of the solution was di-

Copyright © 1987, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1987.0350508 Published online by Cambridge University Press

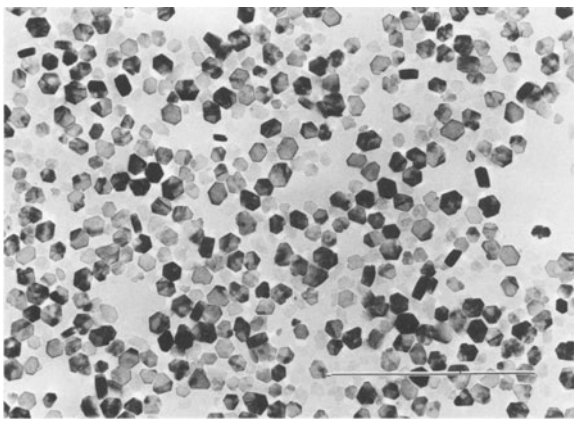


Figure 1. Transmission electron micrograph of gibbsite formed in the solution having an Si/Al ratio of 0 and an NaOH/Al ratio of 2.00. Scale marker = 1 μm.

alyzed against distilled water to remove unreacted silicic acid, monomeric aluminum, and NaCl until the Cl^- reaction with $AgNO_3$ became negative. Part of the dialyzed solution was used for electron microscopy; the remainder was freeze-dried for infrared spectroscopy (IR). The IR spectra were obtained from KBr disks incorporating the freeze-dried materials.

For electron microscopy, a drop of the solution was dried on a microgrid and examined in the JEM 100-B electron microscope operated at 100 kV. The remainder was digested in 0.05 M HCl for 30 min at room temperature to dissolve noncrystalline components and passed through a Millipore filter having a pore size of 0.025 μm. The solid product collected on the filter was resuspended in water and again examined in the electron microscope.

RESULTS

Although special care was taken to avoid contamination with microorganisms, colonies of fungi were noticed in three solutions after 1 year. These three solutions were abandoned, and the data from them were excluded from this paper. In other solutions no microorganisms were detected even after 7 years.

Solutions having Si/Al molar ratios of 0 and 0.266 became slightly opalescent after 20–30 days of aging. Platy hexagonal crystals of gibbsite were identified in these solutions.[1] Figure 1 shows an electron micrograph of gibbsite formed in the solution having an Si/Al ratio of 0 and an NaOH/Al ratio of 2.00. The average diameter of the crystals (about 0.1 μm) did not seem to depend on the NaOH/Al ratio. The gibbsite found in solutions having an Si/Al ratio of 0.266 was similar in shape, but its average diameter was significantly larger (about 0.2 μm). All solutions having Si/Al ratios >0.266 were clear, and no precipitate was noted even after 7 years.

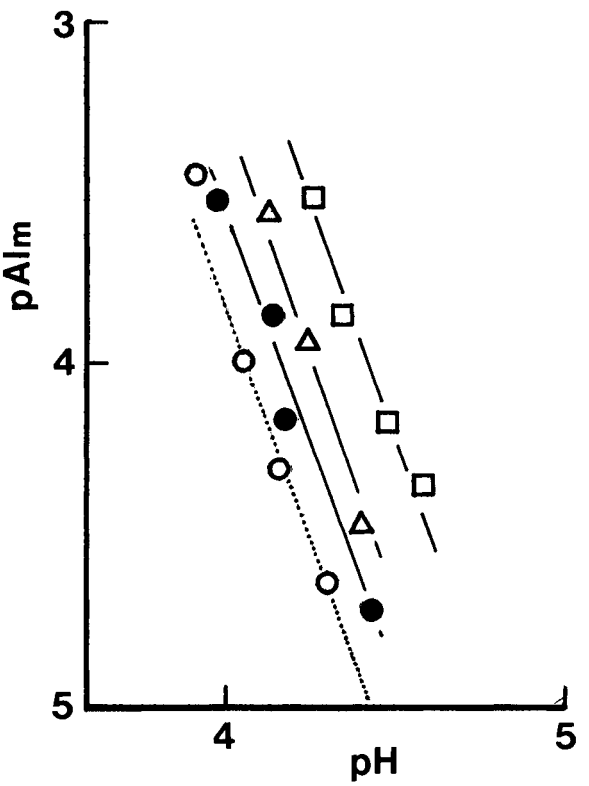


Figure 2. Relationship between negative logarithm of monomeric aluminum ion concentration (pAl_m) and pH of the solutions having Si/Al ratios of 0 (○), 0.266 (●), 0.531 (□), and 4.24 (△). The dotted line shows the solubility of gibbsite.

Figure 2 shows the relationship between pH and pAl_m for solutions having Si/Al ratios of 0, 0.266, 0.531, and 4.24 aged for 7 years, where pAl_m is a negative logarithm of monomeric aluminum ion concentration. The plots for other solutions having different Si/Al ratios were similar and fell in the intermediate region between the curves for solutions having Si/Al ratios of 0.531 and 4.24. The four curves in Figure 2 are similar to those reported by Wada and Wada (1980) for solutions having the same Si/Al and NaOH/Al ratios as the present solutions and which were aged for 100 days at 25°C. The present curves, however, plot in the more acidic region by about 0.5 pH unit.

The dotted line in Figure 2 indicates the solubility of gibbsite calculated from the solubility product of $10^{-33.94}$ (Singh, 1974). A comparison of this curve with the experimental curves in Figure 2 shows that solutions having an Si/Al ratio of 0 were nearly at equilibrium with respect to gibbsite and that the solutions having an Si/Al ratio of 0.266 were supersaturated with respect to gibbsite, despite the presence of even larger

[1] These are not true solutions in a strict sense but suspensions or sols. For simplicity, however, they are termed solutions in this paper.

https://doi.org/10.1346/CCMN.1987.0350508 Published online by Cambridge University Press

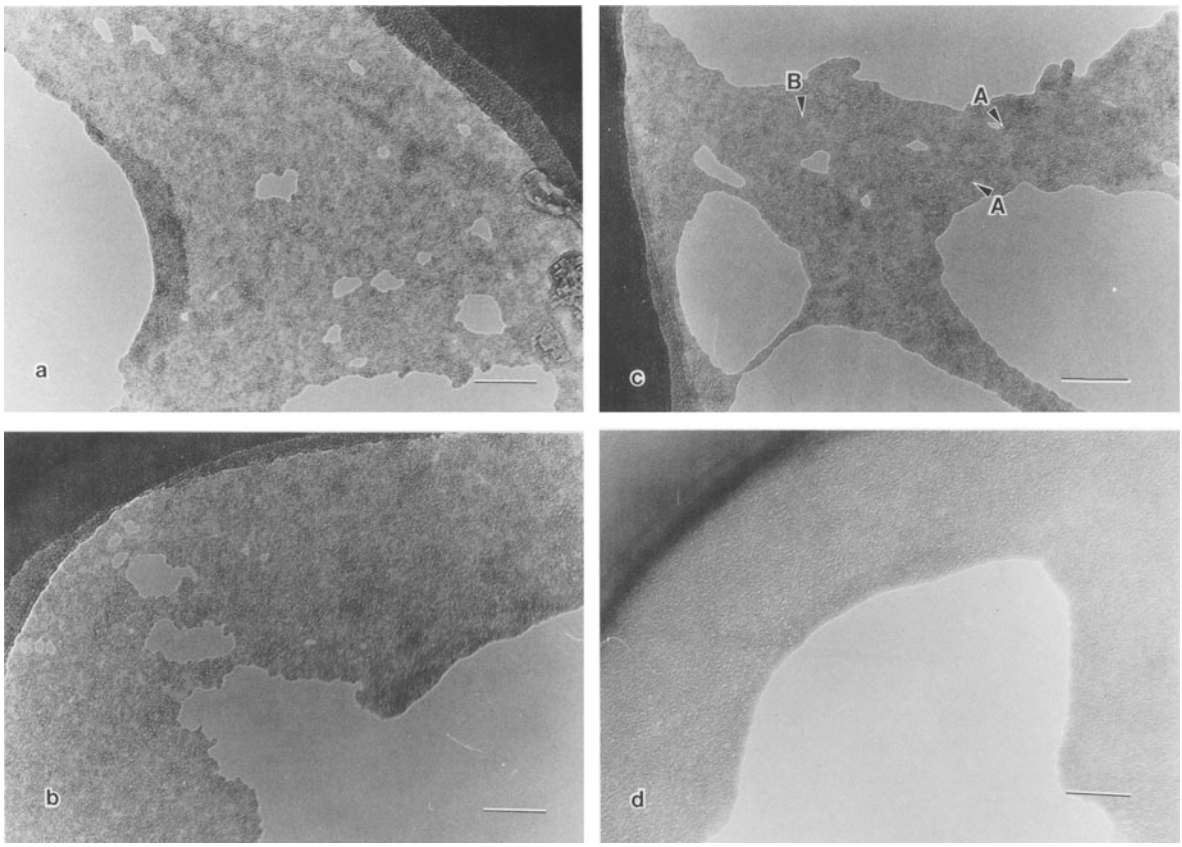


Figure 3. Transmission electron micrographs of the products from solutions having Si/Al ratios of 0.531 (a), 1.04 (b), 2.18 (c), and 4.24 (d). NaOH/Al ratio = 2.00. Arrows A and B in plate (c) indicate parallel lines and rings, respectively. For explanation, see text. Scale marker = 500 Å.

crystals of gibbsite. All solutions having Si/Al ratios >0.266 were apparently supersaturated with respect to gibbsite.

Figure 3 shows transmission electron micrographs (TEM) of the products formed in solutions having Si/Al ratios of 0.531, 1.04, 2.18, and 4.24 and an NaOH/Al ratio of 2.00. The products from the solutions having the same Si/Al ratio but different NaOH/Al ratios had similar morphologies and are not shown in the illustration. Figures 3a and 3b show that imogolite formed in solutions having Si/Al ratios of 0.531 and 1.04. Some structural units of imogolite formed in these solutions were as long as 1 μm, but others were much shorter. The presence of imogolite structural units is not readily apparent in Figure 3c, but close examination shows the presence of short tubes of imogolite that appeared as parallel lines (arrow A), 200–300 Å in length. In addition to the very short parallel lines, numerous rings, about 20 Å in diameter, can be seen in Figure 3c (arrow B). These rings are probably cross sections of tubular structural units that are aligned parallel to the electron beam. Similar short tubes of synthetic Ge-imogolite were described by Wada and Wada (1982). Allophane, a short-range ordered aluminum silicate commonly accompanying imogolite in weathered volcanic ejecta, has been described as rings under an electron microscope. The diameter of the rings for allophane was reported to be in the range 35–55 Å (Kitagawa, 1971; Henmi and Wada, 1976), which is significantly larger than the present one. Figure 3d shows that no imogolite is present in the product from solutions having an Si/Al ratio of 4.24.

Figure 4 shows TEMs of imogolite that remained after solutions having a Si/Al ratio of 0.531 were digested in 0.05 M HCl. The 0.05 M HCl apparently dissolved poorly ordered aluminum silicates and some of the short structural units of imogolite, leaving well-developed units. Similar TEMs were obtained on products from solutions having Si/Al ratios of 1.04 and 2.18, but not for those having a Si/Al ratio of 4.24. Only a trace of imogolite remained after the HCl treatment of solutions having a Si/Al ratio of 2.18. The electron diffraction pattern of threads of the structural unit was a series of ring reflections at 4.1, 3.7, 3.3, 2.3, 2.1, and 1.4 Å, which correspond to the 12, 32, 42, 63, 04, and 06 reflections of natural imogolite (Cradwick

https://doi.org/10.1346/CCMN.1987.0350508 Published online by Cambridge University Press

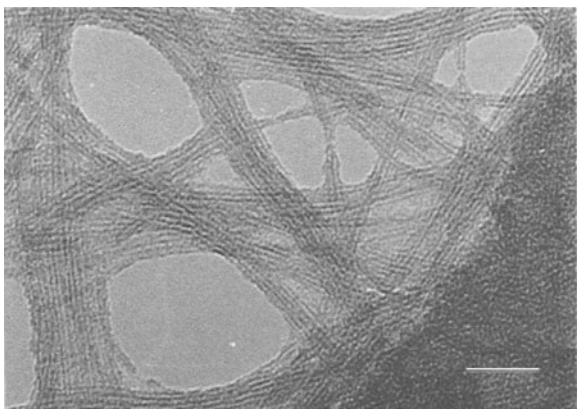


Figure 4. Transmission electron micrograph of purified imogolite formed in a solution having an Si/Al ratio of 0.531. Scale marker = 200 Å.

et al., 1972). Although the resolution of the 42, 32, and 12 reflections was poor, this synthetic imogolite seems to be the first to show the separate 42, 32, and 12 reflections. The diameter of the structural unit measured on isolated particles in some micrographs was 23 ± 2 Å. These data suggest that the imogolite formed in the present solutions at 25°C is similar to that formed in nature.

Figure 5 shows the IR spectra of the freeze-dried products. The products from solutions having Si/Al ratios of 0 and 0.266 gave spectra characteristic of gibbsite. Both spectra were similar, but the shoulder at 1100 cm^{-1} in the spectrum of the former was missing in that of the latter, and the presence of aluminosilicates was not identified in that of the latter. The spectra of the products from solutions having Si/Al ratios of 0.531, 1.04, and 2.18 showed strong absorptions centered at about 950 cm^{-1}, as well as relatively strong and broad absorptions centered at 570 cm^{-1}, with two shoulders at 690 and 500 cm^{-1}, and a weak but relatively sharp absorption at 430 cm^{-1}. The spectrum of the product from the solution having an Si/Al ratio of 4.24 was similar to the products from solutions having smaller Si/Al ratios, but the shoulder at 500 cm^{-1} was missing and the absorption at 430 cm^{-1} was weak and broader.

The dotted line in Figure 5 shows the spectrum of the natural, well-developed imogolite. The spectra of products from solutions having Si/Al ratios of 0.531, 1.04, and 2.18 are similar to that of the natural imogolite in the region 800–400 cm^{-1}, indicating that most of the nonfibrous material in these products also has an imogolite-like structure. On the other hand, the spectrum of the product from the solution having an Si/Al ratio of 4.24 is different from that of natural imogolite in that the absorption at 500 cm^{-1} is missing and the band at 430 cm^{-1} is weak and diffuse. These features are characteristic of the spectra of allophanes having relatively high Si/Al ratios (>0.8) and which probably contain condensed silicate units on Al-octahedral sheets (Parfitt *et al.*, 1980).

DISCUSSION

Wada *et al.* (1979) synthesized boemite, imogolite, and allophane by heating solutions having Si/Al ratios ranging from 0 to 4 and NaOH/Al ratios ranging from 1 to 3 at 95°–100°C. A comparison of the present experimental results with those of Wada *et al.* (1979) suggests that temperature greatly affects the reaction rate. Appreciable imogolite can be obtained in a few days from solutions having Si/Al ratios of about 0.5 at 90°–100°C (Farmer *et al.*, 1977; Farmer and Fraser, 1978; Wada *et al.*, 1979), but only a trace of imogolite formed at 25°C from solutions having a comparable Si/Al ratio (Figure 3a).

Temperature also affects the stability of minerals. Wada *et al.* (1979) obtained boemite from solutions having low Si/Al ratios (<0.5), but in the present synthesis at 25°C, only gibbsite formed in solutions having comparable Si/Al ratios, probably due to differences in the thermodynamic stability of the two minerals, i.e., gibbsite is more stable than boemite at temperatures of <90°C at 1 atm (Chesworth, 1972).

The present results indicate that the stability of imogolite is also affected by temperature. At 95°–100°C, Wada *et al.* (1979) obtained a significant amount of imogolite from solutions having Si/Al ratios as high as 4.0. On the contrary, in the present work at 25°C, no imogolite was found in solutions having an Si/Al ratio of 4.24. IR spectra of the products from the latter solutions were closer to that of allophane having a relatively high Si/Al ratio than to that of imogolite. Furthermore, only a trace of imogolite formed in the solutions having an Si/Al ratio of 2.18, and the structural unit of imogolite that did form was very short (Figure 3c). These data indicate that the range of silicic acid concentration in which imogolite was stable was significantly narrower at 25°C than at 95°–100°C. This conclusion is consistent with the thermodynamic prediction based on the measurement of equilibrium silicic acid concentration over imogolite and boemite at 100°–155°C (Farmer *et al.*, 1979).

In the present experiment, the concentration of monomeric silicic acid in the solutions after 7 years of aging was not measured. Wada and Wada (1980) prepared solutions in which the Si/Al and NaOH/Al ratios were the same as those of the present experiment and reported monomeric silicic acid concentration after 10, 30, and 100 days of aging. Their experimental results showed that the amount of silicic acid incorporated into aluminosilicates gradually increased for 30 days and became nearly constant thereafter. Therefore, the monomeric silicic acid concentration in a 7-year aged solution should be about the same as that in the 100-day aged solution having corresponding Si/Al and

https://doi.org/10.1346/CCMN.1987.0350508 Published online by Cambridge University Press

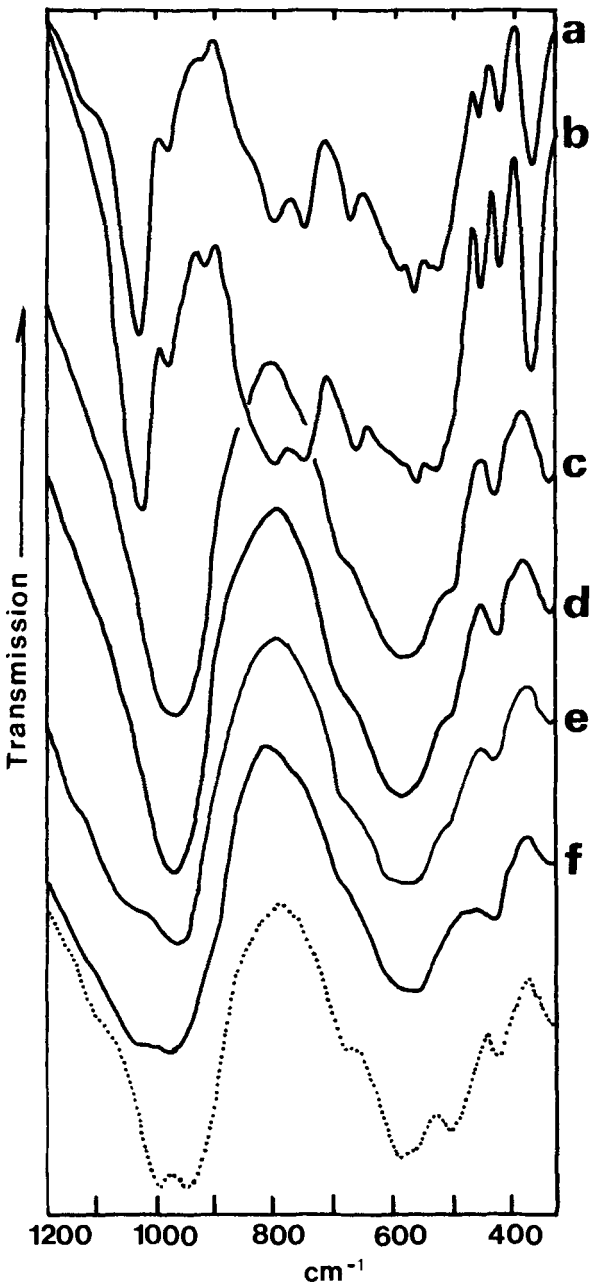


Figure 5. Infrared spectra of the freeze-dried products from solutions having Si/Al ratios of (a) 0, (b) 0.266, (c) 0.531, (d) 1.04, (e) 2.18, and (f) 4.24. NaOH/Al ratio = 2.00. Dotted line shows the spectrum of a natural imogolite.

NaOH/Al ratios. On this basis, the concentration of monomeric silicic acid in the present solutions was calculated using the experimental data of Wada and Wada (1980); the results are summarized in Table 1. The data in this table and the fact that well-developed imogolite was found in solutions having Si/Al ratios of 0.531 and 1.04 indicate that the concentration range of monomeric silicic acid favorable for imogolite formation at 25°C was 0.06–0.4 mM at pH 4–4.5. These concentrations bracket the equilibrium concentration of 0.1 mM for gibbsite-imogolite coexistence at 25°C estimated by Farmer and Fraser (1982).

Table 1. Calculated equilibrium monomeric silicic acid concentration in the solutions aged for 7 years.

Si/Al ratio of starting solution	Average Si/Al ratio of the products[1]	Monomeric silicic acid concentration (mM)[2]
0	0	0
0.266	—	—
0.531	0.40	0.058–0.19
1.04	0.46	0.28–0.43
2.18	0.66	0.68–0.89
4.24	0.90	1.5–1.8

[1] Wada and Wada (1980).
[2] The higher and lower values are the concentrations in solutions with the NaOH/Al ratios of 1.00 and 2.75, respectively.

The external diameter of the structural unit of imogolite synthesized at 25°C estimated from electron micrographs was 23 ± 2 Å, but the images of individual structural units in the micrographs were diffuse and it was often difficult to define the diameter on the micrographs. For this reason, natural imogolite and that synthesized at 100°C were used as reference samples in the present study and were examined in the electron microscope under the similar focusing condition. The estimated external diameters were 21 ± 2 Å for natural imogolite and 28 ± 1 Å for the imogolite synthesized at 100°C. From these data the external diameter of the imogolite synthesized in the present study must be close to that of natural imogolite. A suspension of solid products remaining after the 0.05 M HCl-digestion was dried on a glass slide and examined by XRD. No measurable peak was observed, probably due to an insufficient amount of the specimen.

Cradwick *et al.* (1972) proposed that the wall of the tubular structural unit of imogolite consists of a curved single sheet of gibbsite wherein the OH groups of the internal vacant sites are replaced with O_3SiOH groups. The curvature of the structural unit is caused by the shortening of O–O distances around internal vacant sites, from about 3.2 Å in gibbsite to less than 3 Å, appropriate for an edge of an SiO_4 tetrahedron. These dimensions suggest that the misfit between the vacant site and SiO_4 tetrahedron determines the curvature of the structural unit. The smaller curvature and the resulting larger diameter of the Ge-imogolite (Wada and Wada, 1982) supports the above view, because the O–O distance in a GeO_4 tetrahedron is larger than that in an SiO_4 tetrahedron. A possible reason for the observed temperature-induced increase in diameter of the structural unit of the synthetic imogolite from 23 ± 2 Å at 25°C to 28 ± 1 Å at 100°C is, therefore, the thermal elongation of Si–O bonding in monomeric silicic acid in the reacting solutions at 100°C.

https://doi.org/10.1346/CCMN.1987.0350508 Published online by Cambridge University Press

REFERENCES

Chesworth, W. (1972) The stability of gibbsite and boemite at the surface of the earth: *Clays & Clay Minerals,* **20,** 369–374.

Cradwick, P. D. G., Farmer, V. C., Russell, J. D., Masson, C. R., Wada, K., and Yoshinaga, N. (1972) Imogolite, a hydrated aluminium silicate of tubular structure: *Nature Phys. Sci.* **240,** 187–189.

Farmer, V. C., Fraser, A. R., and Tait, J. M. (1977) Synthesis of imogolite: A tubular aluminium silicate polymer: *J. Chem. Soc. Chem. Comm.* **13,** 462–463.

Farmer, V. C. and Fraser, A. R. (1978) Synthetic imogolite, a tubular hydroxyaluminium silicate: in *Proc. Int. Clay Conf., Oxford, 1978,* M. M. Mortland and V. C. Farmer, eds., Elsevier, Amsterdam, 547–553.

Farmer, V. C. and Fraser, A. R. (1982) Chemical and colloidal stability of sols in the Al_2O_3-Fe_2O_3-SiO_2-H_2O system: Their role in podzolization: *J. Soil Sci.* **33,** 733–742.

Farmer, V. C., Smith, B. F. L., and Tait, J. M. (1979) The stability, free energy and heat of formation of imogolite: *Clay Miner.* **14,** 103–107.

Henmi, T. and Wada, K. (1976) Morphology and composition of allophane: *Amer. Mineral.* **61,** 379–390.

Inoue, K. and Huang, P. M. (1985) Influence of citric acid on the formation of short-range ordered aluminosilicates: *Clays & Clay Minerals* **33,** 312–322.

Kitagawa, Y. (1971) The "unit particle" of allophane: *Amer. Mineral.* **56,** 465–475.

Parfitt, R. L., Furkert, R. J., and Henmi, T. (1980) Identification and structure of two types of allophane from volcanic ash soils and tephra: *Clays & Clay Minerals* **28,** 328–334.

Singh, S. S. (1974) The solubility product of gibbsite at 15, 25, and 35°C: *Soil Sci. Soc. Amer. Proc.* **38,** 415-417.

Tait, J. M., Yoshinaga, N., and Mitchell, B. D. (1978) The occurrence of imogolite in some Scottish soils: *Soil Sci. Plant Nutr.* **24,** 145–151.

Wada, K., Henmi, T., Yoshinaga, N., and Patterson, S. H. (1972) Imogolite and allophane formed in saprolite of basalt on Maui, Hawaii: *Clays & Clay Minerals* **20,** 375–380.

Wada, S.-I. (1986) Modification of 8-quinolinolate extraction method for determination of monomeric aluminum ions: *Jap. J. Soil Sci. Plant Nutr.* **57,** 506–508 (in Japanese).

Wada, S.-I., Eto, A., and Wada, K. (1979) Synthetic allophane and imogolite: *J. Soil Sci.* **30,** 347–355.

Wada, S.-I. and Wada, K. (1980) Composition and structure of hydroxy-aluminosilicate ions: *J. Soil Sci.* **31,** 457–467.

Wada, S.-I. and Wada, K. (1982) Effect of substitution of germanium for silicon in imogolite: *Clays & Clay Minerals* **30,** 123–128.

Yoshinaga, N., Nakai, M., Minagawa, T., and Henmi, T. (1984) Formation of imogolite and allophane in shattered sandstone underlying brown forest soil: *Soil Sci. Plant Nutr.* **30,** 555–567.

(Received 12 September 1986; accepted 2 April 1987; Ms. 1610)

https://doi.org/10.1346/CCMN.1987.0350508 Published online by Cambridge University Press