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Dehydration of Allophane and Its Structural Formula

YASUO KITAGAWA

Department of Soils and Fertilizers, National Institute of Agricultural Sciences,
Nishigahara, Kita-Ku, Tokyo 114, Japan

Abstract

The water in allophane from 2 localities in Japan (Misotsuchi bed at Iijima, Nagano, and Kanumatsuchi bed at Kanuma, Tochigi) was studied by thermal analysis, infrared absorption spectroscopy, and X-ray diffraction. The water in the allophanes was divided into adsorbed water and structural hydroxyl groups by resolving the differential of the thermogravimetric curves into two gamma distributions.

Computed weight percentages of the types of water in the Misotsuchi and Kanumatsuchi allophanes are: adsorbed water 23.2 and 23.0, respectively, and structural hydroxyl 10.6 and 11.2. Omitting the adsorbed water, the hydroxyl groups compose 13.9 and 14.6 wt percent of the allophanes. These values are close to the 13.96 percent for kaolinite.

The structural formulae obtained from these results and chemical analyses are, for Misotsuchi allophane,

$$Si_{1.38}(Al_{1.98}Fe_{0.02})O_{3.94}(OH)_{3.46}(OM)_{0.20}\cdot 3.78H_2O$$

and, for Kanumatsuchi,

$$Si_{1.45}(Al_{1.98}Fe_{0.02})O_{3.95}(OH)_{3.72}(OM)_{0.16}\cdot 3.80H_2O$$

where M represents bases.

Introduction

The properties of water in allophane pose an interesting and important problem. Since the work of Ross and Kerr (1934), many scientists have pointed out that water in allophane is released over a wide temperature range from room temperature to near 1000°C, and that it is difficult to distinguish between adsorbed water and structural hydroxyl groups. Results obtained from substitution of hydroxyls by fluorine, deuterium exchange, infrared absorption spectroscopy, and nuclear magnetic resonance spectroscopy show that: (1) the structural hydroxyl groups in allophane are unstable, compared with those in kaolin minerals and others, (2) all the hydroxyl groups are on the surface, and (3) there is a continuous exchange of protons between adsorbed water and the structural hydroxyl groups (Egawa, Sato, and Nishimura, 1960; Wada, 1966; Kitagawa, 1972). Birrell and Fieldes (1952) pointed out the irreversible drying of volcanic ash soils. Misono *et al* (1953) perceived the hysteresis between dehydration and rehydration of volcanic ash soils. The phenomenon was explained by Kitagawa (1971) from his conclusion that allophane consists of fine "unit particles" which are cemented together on drying.

In this paper, the water in allophane is divided into the adsorbed form and structural hydroxyl groups, on the basis of the results of thermogravimetry and differential thermogravimetry. The changes of allophane with heating were examined by infrared absorption spectroscopy and X-ray diffraction. The structural formula of allophane was obtained from chemical analysis and the results of thermal analysis.

Samples and Experimental Methods

Allophane samples obtained from two weathered pumice beds—the so-called Misotsuchi bed in Iijima Town, Nagano Prefecture, Japan, and the Kanumatsuchi bed in Kanuma City, Tochigi Prefecture, Japan—were prepared as follows: First, the gel film, composed of "imogolite," was removed from weathered pumice with tweezers. The weathered pumice was suspended in HCl-acid solution at pH 3.5, and the fraction less than 2 μm was siphoned off according to the Stokes' Law. The iron oxide impurities were removed by the dithionate-citrate system buffered with $NaHCO_3$, according to the method of Mehra and Jackson (1959). The treated sample was dried for two weeks in a desiccator over 58 percent H_2SO_4 until the weight was constant. The relative humidity inside the desiccator was about 30 percent, calculated from tables on phase equilibrium (Sasaki, 1966).

The purity of prepared samples was tested by three methods. X-ray diffraction patterns of both samples showed two broad, weak peaks near 3.5 and 2.3 Å (Fig. 2, A) which originated from allophane (Sudo, 1959). Reflections associated with layer silicates were not found even in oriented specimens. Differential thermal curves showed a sharp exotherm at 935°C for the Misotsuchi sample and at 920°C for the Kanumatsuchi, an endotherm near 130°C for both, and no intermediate endotherm for either. These are characteristics of allophane (Van Olphan, 1971). Moreover, imogolite and other impurities could not be recognized in electron micrographs.

Significant alteration of allophane, caused by drying for two weeks over 58 percent H_2SO_4, was not noticed in the X-ray diffraction pattern, infrared absorption spectrum, differential thermal curve, and weight-loss curve.

The weight-loss curve and its differential were obtained by using a Rigaku-Denki Thermoflex thermal analyzer at a heating rate of 10°C/min in ordinary atmosphere from room temperature to 1000°C. A specimen of about 30 mg was packed in a small platinum pan for measurement. The base-line of the curves was obtained by using αAl_2O_3.

The infrared absorption spectrum was measured in the range from 4000 to 400 cm^{-1} by a Hitachi EPI-G2 infrared spectrometer. The tablets for measurement were prepared by pressing a mixture of 1 mg of specimen with 200 mg of KBr at 200 kg/cm^2 after heating at 110, 150, 200, 300, 400, and 600°C for 2 hours. The untreated specimen was also analyzed.

X-ray diffraction patterns of powder specimens were obtained with $CuK\alpha$ radiation at 40 kV, 10 mA, and a scanning speed of $4°(2\theta)/min$.

Silicon, aluminum, iron, and titanium were determined colorimetrically by the molybdenum blue, aluminon, o-phenanthroline, and hydrogen peroxide methods, respectively. Magnesium and calcium were determined by atomic absorption photometry. Potassium and sodium were determined by flame photometry.

Results and Discussion

Thermal Analysis, X-ray Diffraction, and Infrared Adsorption

The weight-loss curves (TG curves) and their differential curves (DTG curves) for both allophanes are shown in Figure 1. The TG curves revealed two kinds of weight loss, a rapid one up to 200°C, and a slow one above 200°C. The DTG curves revealed a sharp, intense peak near 9 min (90°C), and a broad, weak peak centered about 35 min (350°C). The TG and DTG curves obtained with a sample whose weight was about 30 mg hardly varied even when the heating rate was changed to 5 or 20°C/min in measurement.

These curves suggest two types of dehydration in allophane: (1) dehydration of adsorbed water at low temperatures, and (2) "dehydroxylation" of structural hydroxyl groups at high temperatures. This division of water in allophane has been suggested previously by Watanabe and Sugo (1972). The structural hydroxyl groups in allophane may be released too slowly to give a detectable DTA endotherm, no endotherm being observed near 350°C in either allophane.

The X-ray diffraction patterns of allophane from Misotsuchi and Kanumatsuchi are shown in Figure 2. With the rise of heating temperature, the broad peak near 3.5 Å of both allophanes shifts towards 4.0 Å, and the peak near 2.3 Å disappears. These changes are especially noticeable between 300 and

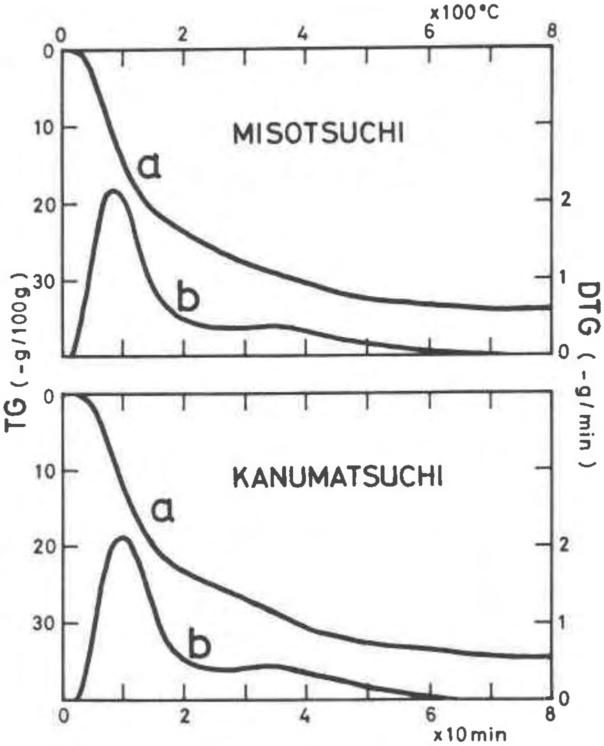

FIG. 1. The TG (a) and DTG (b) curves of allophane separated from Misotsuchi and Kanumatsuchi.

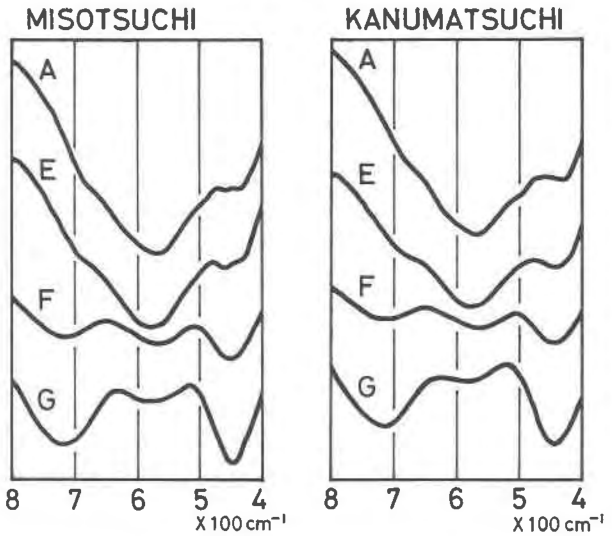

FIG. 2. The changes of IR spectra of allophane separated from Misotsuchi and Kanumatsuchi by heating: **A**, unheated; **E**, 300°C; **F**, 400°C, **G**, 600°C.

400°C. Udagawa, Nakada, and Nakahira (1969) attribute this change to a change of the co-ordination number of Al from 6 to 4 during the dehydration of allophane.

The changes of infrared absorption bands with heating are shown in Table 1. As the heating temperature was raised to 300°C, the maximum of the band associated with O–H stretching vibrations shifted to higher wave-numbers, from 3470 cm^{-1} at room temperature to 3500 at 300°C in Misotsuchi, and from 3460 to 3520 cm^{-1} in Kanumatsuchi allophane. This shift may be ascribed to the release of adsorbed water. In fact, the band at 1630 cm^{-1} associated with O–H deformation vibration was greatly weakened with heating above 200°C; this was not so below 150°C. The maximum of the band associated with the O–H stretching vibration in allophane was reversed toward low wave-numbers with heating above 300°C. As the temperature was raised the maximum of the absorption band near 1000 cm^{-1}, which is associated with Si–O stretching vibration in allophane, was also shifted toward higher frequencies up to 300°C. The data in Table 1 suggest that (1) adsorbed water of allophane is released below 200°C, (2) the structural hydroxyl groups of allophane are released abundantly between 300 and 400°C, and (3) dehydration of adsorbed water strengthens Si–O bonds in allophane.

TABLE 1. Changes of IR Absorption Bands Associated with O–H Vibrations and Si–O Stretching Vibration in Allophanes by Heating

Temp. °C	O-H vibrations stretching, cm^{-1}		O-H vibrations deformation*		Si-O vibration stretching, cm^{-1}	
	(1)	(2)	(1)	(2)	(1)	(2)
Unheated	3470	3460	1.0	1.0	980	970
110	3480	3480	0.8	0.7	990	980
150	3480	3500	0.7	0.6	990	990
200	3500	3520	0.3	0.3	1000	990
300	3500	3520	0.2	0.2	1000	1000
400	3450	3470	0.1	0.1	1000	1000
600	–	–	0.0	0.0	1000	1000

*Relative intensity of O-H deformation vibration: untreated, 1.0.
(1) Misotsuchi allophane. (2) Kanumatsuchi allophane.

The infrared absorption spectra of allophane in the region ranging from 800 to 400 cm^{-1} were also changed with heating (Fig. 3). The band at 570 cm^{-1} was unchanged at 300°C but weakened at 400°C, and the bands at 720 and 450 cm^{-1} appeared clearly above 400°C. Although these bands are not identified, the spectra are noticeably changed between 300 and 400°C, which is in agreement with the preceding data.

Static methods, such as the experiments on changes of infrared absorption spectra and X-ray diffraction patterns produced by heating, cannot compare directly with dynamic methods such as TG and DTG. However, the changes in infrared absorption spectra and X-ray diffraction patterns strongly indicate the alteration of allophane with dehydration.

Analysis of DTG Curves

DTG curves of allophane show two types of dehydration: dehydration of adsorbed water and de-

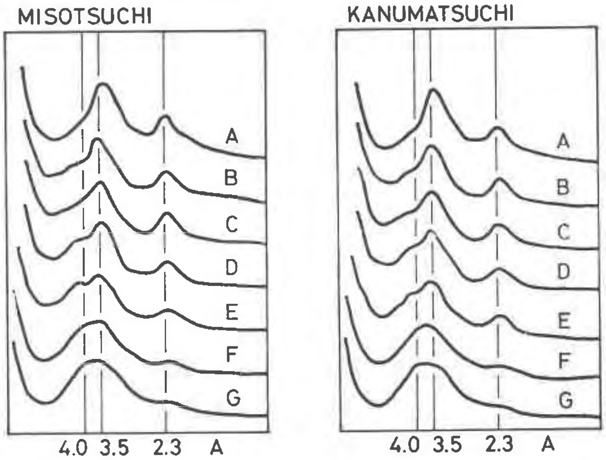

FIG. 3. The changes of X-ray diffraction patterns of allophane separated from Misotsuchi and Kanumatsuchi by heating: **A**, unheated; **B**, 110°C; **C**, 150°C; **D**, 200°C; **E**, 300°C; **F**, 400°C; **G**, 600°C.

hydroxylation of structural hydroxyl groups. From the shape of the DTG curves (curves **b**, Fig. 1), the right side of the peaks (9 and 35 min) originating from each type of dehydration were presumed to tail toward the high temperature region. Consequently, a bell-shaped curve was not applied to the DTG peak. The formula, $y = cx^{N-1}e^{-x/a}$, integration of which corresponds to a gamma function, was assumed to simulate each peak of the DTG curve observed. The parameters, a, c, and N, were computed and are shown in Table 2, where "curve I" indicates the parameters for the function associated with the dehydration of adsorbed water and "curve II" those for structural hydroxyl groups. The multiple correlation coefficient between the computed and observed DTG curves was $R = 0.997$ for both samples. This value is nearly 1.0. Accordingly, the simulation of DTG curves of allophane by the formula is mathematically significant.

The computed TG and DTG curves of allophanes are shown in Figure 4, where the dashed lines show curves I and II, and the solid lines indicate the curves **a** and **b** synthesized from their respective curves I and II. The computed curves accurately reproduce the observed curves. Curve I of DTG is drawn over the range from room temperature to 300°C and almost terminates near 200°C. Curve II is drawn over a wide range, from 100 to 700°C. The maximum of each DTG curve is about 90°C for curve I, and about 320°C for curve II, in both allophanes.

The areas of the DTG curves were calculated with the continued product of parameters c, a, and $\Gamma(N)$, and are shown in the bottom of Table 2; $\Gamma(N)$ is $(N-1)!$ and is obtained from tables of the gamma function. These values correspond to the amount of adsorbed water (curve I) and structural hydroxyl groups (curve II); the weight percentage of adsorbed water is 23.2 for Misotsuchi and 23.0 for Kanumatsuchi allophane, and that of structural hydroxyl is 10.6 and 11.2, respectively.

TABLE 2. The Parameters of the Function $y = cx^{N-1}e^{-x/a}$ Simulating the Dehydration of Allophane, and the Area Obtained from Its Integral

	Misotsuchi		Kanumatsuchi	
	curve I	curve II	curve I	curve II
Parameters				
N	2.11	4.20	1.87	3.33
a	4.97	8.57	6.15	9.80
c	2.48×10^{-2}	2.99×10^{-9}	3.15×10^{-3}	1.13×10^{-11}
Γ(N)	2.30×10^{1}	1.62×10^{4}	1.55×10^{2}	2.27×10^{6}
Area				
c·a·Γ(N)	23.2	10.6	23.0	11.2

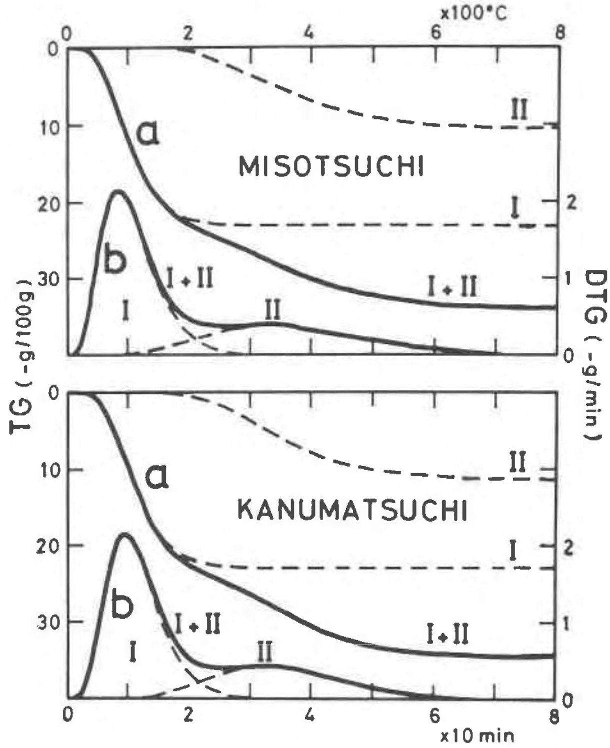

FIG. 4. The TG (**a**) and DTG (**b**) curves of Misotsuchi and Kanumatsuchi allophane calculated from Γ function: **I**, the curves associated with the dehydration of adsorbed water; **II**, the curves associated with the dehydroxylation of structural hydroxyl group; **I + II**, the curves synthesized from **I** and **II**.

Omitting the adsorbed water, the structural hydroxyl groups compose 13.9 percent (by weight) of the Misotsuchi allophane and 14.6 percent of the Kanumatsuchi. These percentages are close to the 13.96 percent hydroxyl present in kaolinite, $Si_2Al_2O_5(OH)_4$. Udagawa, Nakada, and Nakahira (1969) and Kitagawa (1973a) have previously suggested the structural similarity of allophane to kaolin minerals.

Structural Formula of Allophane

Ossaka (1960) proposed a general formula for allophane, $(SiO_2)_{1-2}Al_2O_3\cdot5H_2O$, from consideration of chemical analyses. Iimura (1969) proposed a structural formula $(OH)_{0.86}O_{1.61}Si_{1.33}O_{1.23}Al_{2.00}(OH)_{4.77}$, on the basis of chemical analysis, thermogravimetry, and the characteristics of ion exchange.

The structural formulae of allophanes from Misotsuchi and Kanumatsuchi beds were constructed from their chemical compositions (Table 3). The

TABLE 3. Chemical Composition and Structural Formula of Allophanes

Chemical composition*, Wt. %	(1)	(2)
SiO_2	28.31	29.17
TiO_2	0.40	0.42
Al_2O_3	34.41	33.81
Fe_2O_3	0.56	0.56
MgO	0.08	0.04
CaO	tr	tr
K_2O	0.29	0.16
Na_2O	1.91	1.48
$+H_2O$**	10.60	11.20
$-H_2O$**	23.20	23.00
Total	99.76	99.81

Structural formula

(1) $Si_{1.38}(Al_{1.98}Fe_{0.02})O_{3.94}(OH)_{3.46}(OM^{***})_{0.20}\cdot 3.78H_2O$

(2) $Si_{1.45}(Al_{1.98}Fe_{0.02})O_{3.95}(OH)_{3.72}(OM^{***})_{0.16}\cdot 3.80H_2O$

*Analyst: The author.
**$+H_2O$ and $-H_2O$ obtained by analysis of DTG curves.
***M represents bases.
(1) From Misotsuchi bed, Iijima, Nagano, Japan.
(2) From Kanumatsuchi bed, Kanuma, Tochigi, Japan.

total H_2O was split into structural hydroxyl ($+H_2O$) and adsorbed water ($-H_2O$) by the preceding mathematical analysis of DTG curves. The molecular ratios of the total water *vs* alumina are 5.51 for Misotsuchi and 5.66 for Kanumatsuchi. This agrees with the result obtained by Yoshinaga (1966). However, the ratios $+H_2O/Al_2O_3$, 1.73 for Misotsuchi and 1.86 for Kanumatsuchi are lower than the values 2.31 to 2.81 obtained by Yoshinaga. Recently, Okada *et al* (1972) stated that the molecular ratio, $+H_2O/Al_2O_3$, of allophane is about 2.00.

The structural formulae of the two allophanes are quite similar (Table 3). Allophane consists of Si, Al, Fe, H, O, and bases. Iron is included as a constituent of allophane, but Ti is omitted (Yoshinaga, 1966; Kitagawa, 1973b). Bases are believed to exchange for part of the hydrogen in structural hydroxyl groups of allophane. The sum of Al and Fe is set at 2.00.

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