THE WEATHERING PROCESSES OF VOLCANIC ASH AND PUMICE DEPOSITS IN HOKKAIDO

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CONTENTS

I. Introduction

In Hokkaido, the northernmost island of Japan, where Quaternary volcanoes of the Kuril, Daisetsu, Nasu and Chôkai volcanic zones are distributed, a number of pyroclastic deposits of late Pleistocene to Recent are widely developed, especially in its southern part. During the last thirty years, their distribution, source, age of eruption and modes of emplacement have been studied in detail by many geologists and pedologists[28-30], resident in Hokkaido, for one thing in order to increase the agricultural productivity, and for another to decide the nature of volcanic activity. Consequently great advance has been made in the

volcano-stratigraphical studies, especially in those of the late Pleistocene to Recent[2-6,12-15,20-22]. On the other hand, however, little has been known on inorganic colloids of these pyroclastic deposits from the view point of modern clay mineralogy[10,11,22].

In this paper, the writer has endeavored to identify the clay minerals found in the altered products from these pyroclastic deposits, and to elucidate crystallization processes of volcanic glasses to crystalline materials or hydrated halloysite during the weathering.

II. Volcano-stratigraphical consideration

For the present study sixty-one specimens of clay fraction obtained from eight type localities of these deposits were investigated by several manipulations as described below. The distribution of these deposits and the localities of the samples are shown in Fig. 1.

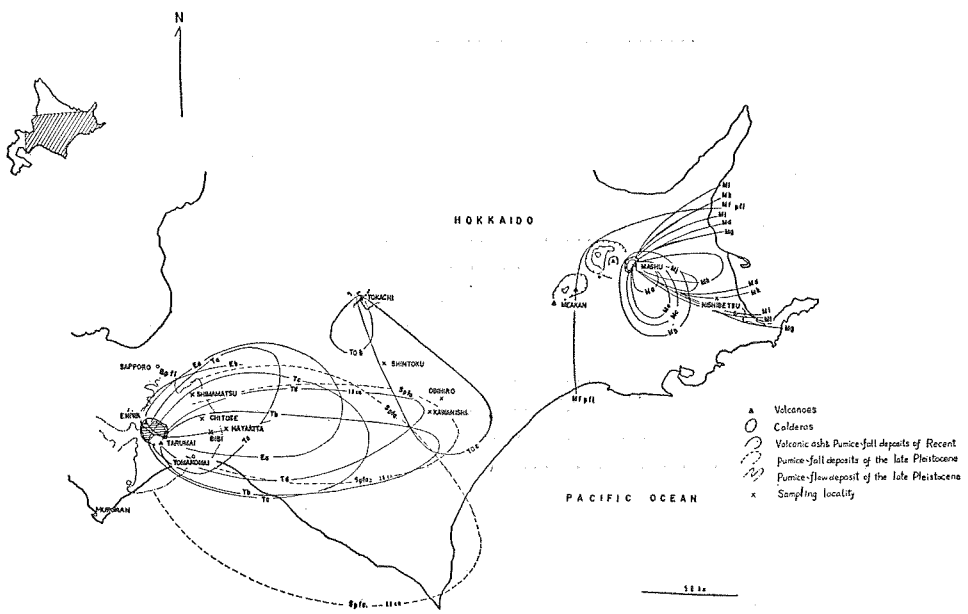

Fig. 1. Distribution of the pyroclastic deposits in Hokkaido, concering to this study and the localities of the samples. The deposits of Recent are drawn after S. Yamada and H. Seo, showing the limit of 10cm, and those of late Pleistocene are drawn after Y. Katsui.

1. Stratigraphical sequence of pyroclastic deposits at Hayakita.

a) Classification and chronological consideration

Eleven beds of pyroclastic deposits are found covering the unconsoli-

dated river terrace deposit at Hayakita, about 4 Km southeast of Chitose city. They are summarized in Table 1.

Table 1. The sequence of pyroclastic deposits at Hayakita.

	Deposit	Index	Age of eruption
Holocene	Tarumai *a* pumice-fall deposit	Ta	1739 A. D.
	Tarumai *b* pumice-fall deposit	Tb	1667 A. D.
	Tarumai *c* pumice-fall deposit	Tc	800–900 yrs. B.P.
	Tarumai *d* pumice-fall deposit	Td	3,000–5,000 yrs. B.P.
	Eniwa *a* pumice-fall deposit	Ea	
	Eniwa *b* pumice-fall deposit	Eb	more than 5,000 yrs. B.P.
late Pleistocene	Shikotsu 1 pumice-fall deposit	$Spfa_1$	20,000 yrs. B.P.
	Shikotsu 2 pumice-fall deposit	$Spfa_2$	
	Shikotsu 5 pumice-fall deposit	$Spfa_5$	
	Shikotsu scoria-fall deposit	Ssfa	
	Shikotsu α pumice-fall deposit	Sα	

Each deposit is subdivided into A-, B-, and C-horizons following the pedological soil profile concept, and their geological column is shown in Fig. 2.

For the weathering processes, the time factor plays an important role. The ages of eruption of these deposits as shown on the right side of geological column are determined by correlating the data of the remains of the stone-age in the deposits, accumulation ratio of the peat within these deposits, the archives of the eruptions in historic time, and carbon 14 dating of the charcoal in these deposits[30]. It is recognized from the field observations that there were some time intervals under the $Spfa_2$ and Ssfa. But the time intervals between the deposits younger than $Spfa_2$ were estimated accuratelly. At Bibi, for instance, a fossil forest of *Picea jezoensis* embeded in $Spfa_1$ was later blasted horizontally by Spfl (Shikotsu pumice-flow deposit[13]*), leaving only the lower parts of trunks, about 10 cm to 30 cm in diameter. Consequently it is supposed that there was a time interval sufficient for the growth of these fossil forest. The length of weathering of all deposits younger than the $Spfa_1$ on the ground surface was calculated from the age of eruption of these deposits, as shown in Table 2.

It is apparent from these table that the lower is the horizon, the

* This deposit is absent at Hayakita, but is distributed at Bibi, Chitose and Shimamatsu as shown in Fig. 1.

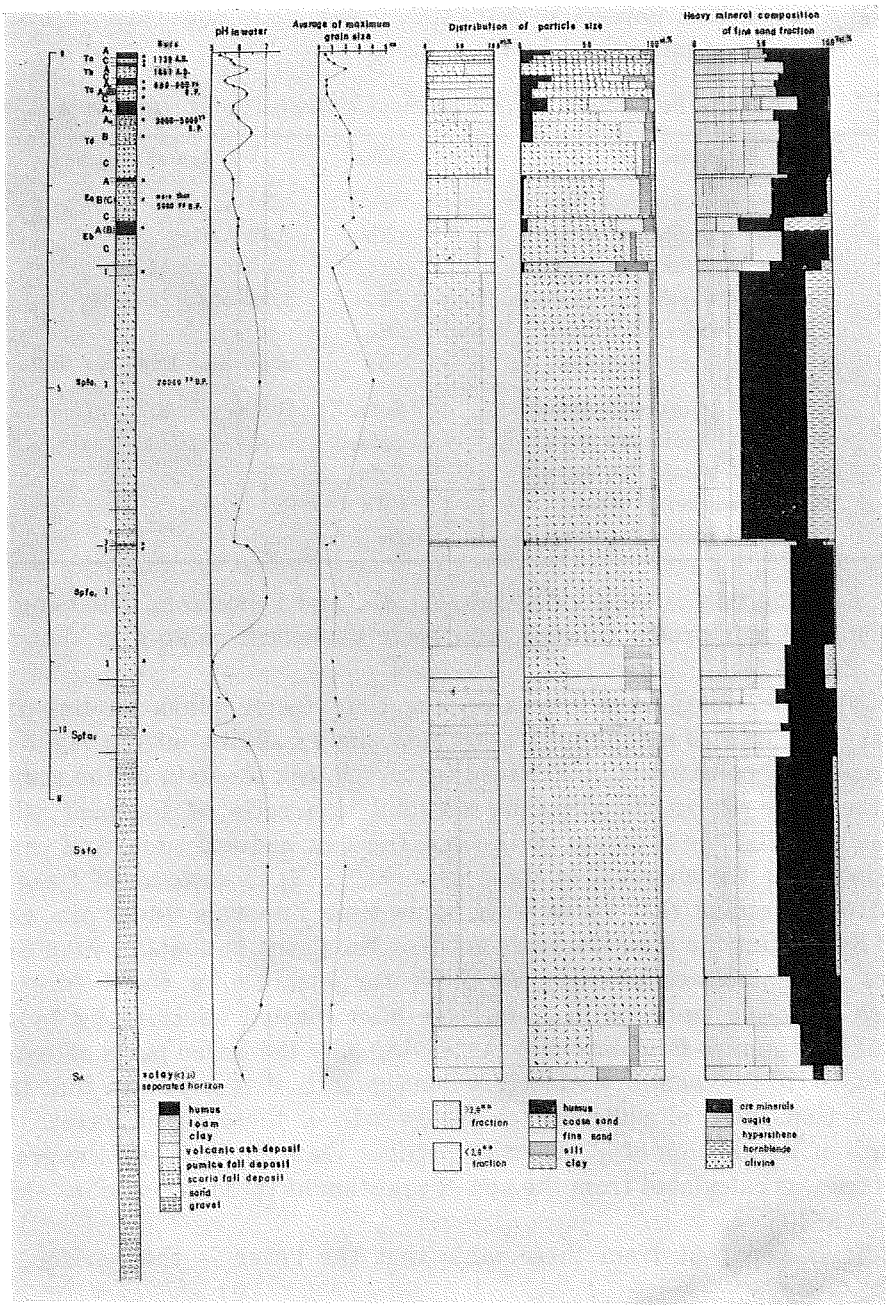

Fig. 2. Columnar section of the pyroclastic deposits at Hayakita

Table 2. The lengh of weathering of each deposits younger than $Spfa_1$.

Ta	221 yrs.**
Tb	72 yrs.
Tc	660 yrs.
Td	3,000-4,000 yrs.
Ea, Eb	more than a few thousands years
$Spfa_1$	more than 10,000 yrs.

** This caluclation was based on 1960 A.D.

longer is the weathering time, with the exception of Tb, the weathering time of which is shorter than that of Ta.

No evidence has been found which indicates that these deposits have not been affected by the post-glacial transgression[15], and that humus is absent in the deposit of $Spfa_1$ which was correlated by M. Minato[18,19] to Tottabetsu-II ice-age or a little younger horizon. This fact may prove the absence of vegetation in the ice-age. Since Eb and Ea were deposited, in the Alluvium soil forming agency has been active.

b) Petrological and some physical properties

The petrological properties of Ssfa, $Spfa_2$ and $Spfa_1$ have been determined by Y. Katsui[14], and those of the other deposits were determined by assemblage of heavy minerals, which were separated by heavy liquid (Thoulet's solution s.g.=2.9), and examined under the microscope. The results are as follows:

S_α: augite-hypersthene andesite, Ssfa: olivine-augite-hypersthene andesite, $Spfa_5$: hornblende-augite-hypersthene dacite, $Spfa_2$: hornblende-augite-hypersthene dacite, $Spfa_1$: augite-hornblende-hypersthene rhyolite, Eb and Ea: augite-hornblende-hypersthene dacite, Td-Ta: augite-hypersthene andesite.

As it is expected that the grain size of the deposits should have given effects on the weathering, the writer has made the mechanical analysis of these deposits. The third column of Fig. 2 shows the average values of ten largest grains on the area of 1 m^2 at the outcrops. It is obvious from this column that the fractions of upper part of these pyroclastic deposits are always smaller than those of lower part. This fact shows that the agency of physical weathering was stronger in the upper part than in the lower, and also that the sorting in the atmosphere was good at the time of eruption.

For the finer fractions less than 2 mm mecanical analysis was made.

The fourth column of Fig. 2 shows the ratio of fractions larger and smaller than 2 mm, and fifth column shows the results of mechanical analysis of finer fractions. Humus was separated chemically†. It is proved from the mechanical analysis, that the clay fractions are very scanty except in Sa and the upper part of $Spfa_5$. Out of thirty-one samples studied, only thirteen have detectable clay fractions, which were used for the mineralogical experiments.

The pH values of these thirty-one samples were measured by colorimetry with the result as shown in the second column of Fig. 2. Except Ssfa and $Spfa_2$, which are neutral, the pH values of these deposits range from 5.0 to 6.8. These values of pH is common to the volcanic ash soils prevailing in Hokkaido. Besides the upper part is more acidic than the lower in each deposit, and therefore it is apparent that the acidic reaction was active on the surface when each deposit was accumulated in the past. There is no evidence that Ca, Mg and Na were concentrated.

2. The sequence and stratigraphy of pyroclastic deposits other than at Hayakita

Besides at Hayakita, the samples were also collected at Bibi, Chitose

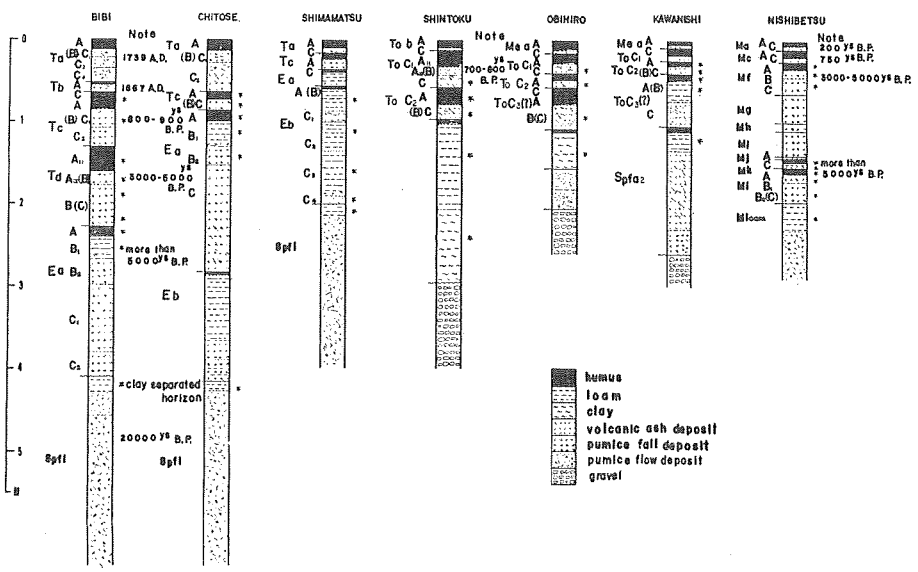

Fig. 3. Columnar section of the pyroclastic deposit other than at Hayakita horizons from which clay was separated.

† after Dr. S. Tsuru.

and Shimamatsu in the Sapporo-Tomakomai lowland district, Shintoku, Obihiro and Kawanishi in the Tokachi district, and Nishibetsu in the Nemuro district (Fig. 1).

The geological columns of these localities are shown in Fig. 3. The sequence of pyroclastic deposits at Bibi, Chitose and Shimamatsu is the same as that of Hayakita except Spfl, which was deposited covering $Spfa_1$ in these localities. The indexes of deposits should be referred to those of Hayakita.

Several pyroclastic deposits and volcanic ashes are recognized, covering the river terrace gravel beds or fan-deposits, in the Tokachi district. They are summarized in Table 3.

Table 3. The sequence of pyroclastic deposits in the Tokachi district.

Deposit	Index	Age of eruption
Tokachi *b* pumice-fall deposit	To b	200 yrs. B.P.
Meakan *a* volcanic ash deposit	Me a	200 yrs. B.P.
Tokachi C_1 volcanic ash deposit	To C_1	700–800 yrs. B.P.
Tokachi C_2 volcanic ash deposit*	To C_2	a few thousands years ago
Tokachi C_3 volcanic ash deposit**	To C_3 (?)	several thousands years ago
Shikotsu 2 pumice-fall deposit***	$Spfa_2$	

* A few remains of Hokuto-type ceramic culture (middle Jomon culture) were found directly below this deposit by Mr. Y. Kondo, and the age of eruption is estimated by this fact.

** Except the fact that this deposit was originated from Tokachi volcano, the distribution and the age of its eruption have not yet been established, and so the writer gives this name temporarily, and roughly estimates the age of its eruption.

*** This deposit is distributed also in the Tokachi district as shown in Fig. 2.

This sequence is not always completely recognized at the outcrops, and the geological columns at these localities are shown in Fig. 3. From the petrological properties of To C_1 and To C_2, and mineral assemblage of the fine sandy parts, they are identified as augite-hypersthene andesite.

In the Nemuro district, the specimens were collected only at one locality of Nishibetsu, where the deposits originated from Mashu volcano are distributed, with the sequence as shown in Table 4 and Fig. 3.

From the petrological properties of these deposits given by Katsui[14], and the mineral assemblage of the fine sandy parts, M loam and Ml are identified as felsic augite-hypersthene andesite, Mk and Mf augite-hypersthene dacitic andesite.

Table 4. The sequence of the pyroclastic deposits at Nishibetsu.

Deposit	Index	Age of eruption
Mashu *a* volcanic ash deposit	Ma	200 yrs. B.P.
Mashu *c* volcanic ash deposit	Mc	750 yrs. B.P.
Mashu *f* pumice-fall deposit	Mf	3,000-5,000 yrs. B.P.
Mashu *g* pumice-fall deposit	Mg	
Mashu *h* pumice-fall deposit	Mh	
Mashu *i* pumice-fall deposit	Mi	
Mashu *j* pumice-fall deposit	Mj	
Mashu *k* volcanic ash deposit	Mk	more than 5,000 yrs. B.P.
Mashu *l* pumice-fall deposit	Ml	
Mashu loam (pumiceous volcanic ash deposit)	M loam	

Ma and Mc were originated from the central cone of Mashu volcano.
Deposits Mf to Mj were all related to the activity which took place just before the Mashu caldera was subsided.
Mk, Ml and M loam were originated from the somma of Mashu volcano.

III. Experiments

1. Separation and preparation of clay specimens

The specimens used for the clay mineralogical experiments were prepared as follows. The samples collected from the outcrops were first air-dried and separated by sieving into two parts over and below 2 mm. The finer parts were then suspended in pure water and the clay fraction ($<2\,\mu$) were collected by using siphon following the Stocke's Low. The humus in the clay fraction was removed by adding 30% peroxide kept at 50°C.

2. Differential thermal analysis

This method is particularly useful for investigating the clay fractions in the altered products of recent pyroclastic deposits, for the weathering products are amorphous and the X-ray diffraction analysis is not so reliable as in the case of crystalline materials.

Heating ratio was 10°C per minute. The differential thermal analysis curves of the specimens collected at Hayakita are shown in Fig. 4. From these curves it is possible to group these specimens as follows:

(1) The specimens of Ta and Tb do not contain allophane or crystalline materials, and mainly consist of unaltered glassy materials. The curve of Ta C shows a strong exothermic peak in the range of 600~700°C.

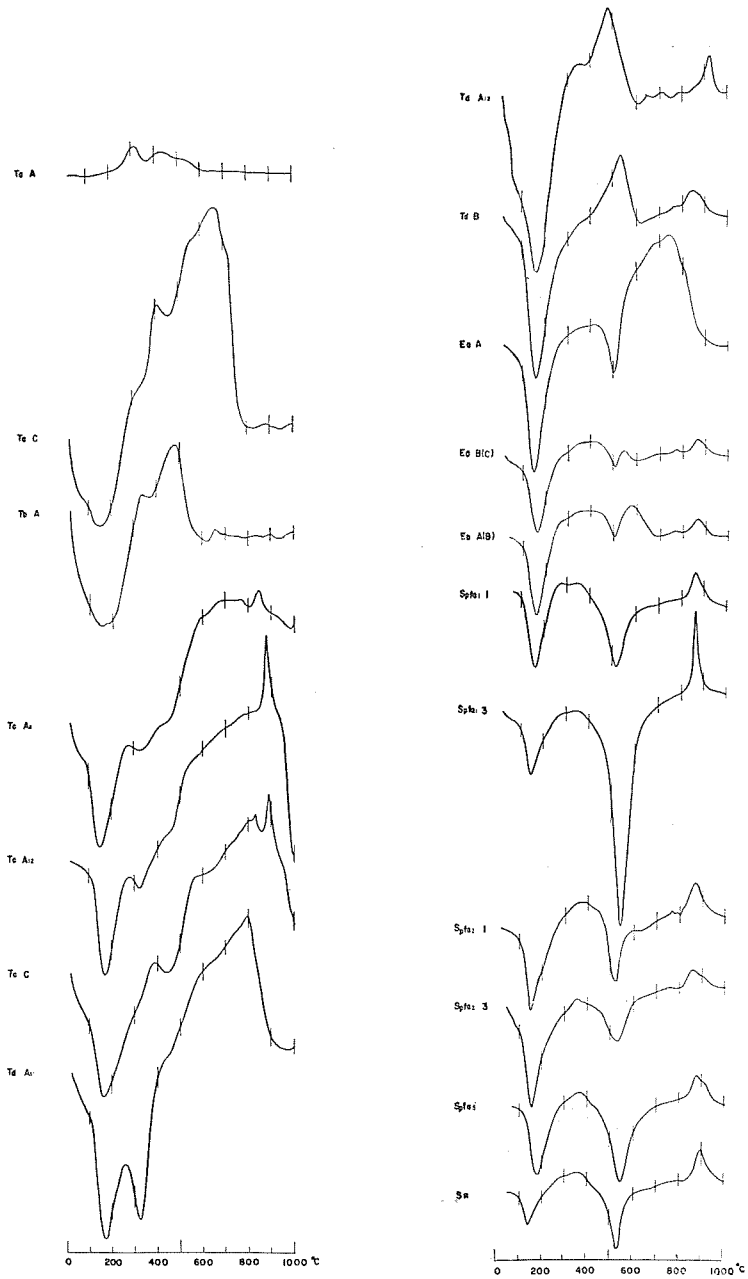

Fig. 4. Differential thermal analysis curves of the specimens at Hayakita

This peak is due to the combined materials of humus, which was not

removed perfectly by the peroxide treatment, and alumina[7]. The exothermic peak of these curves in the region lower than 500°C may be due to the gel-like materials of aluminium hydroxide[7,17].

(2) In the curves of the specimens of Tc and Td, the endothermic peaks in the range of 100~200°C are even sharper, and exothermic peaks in the region higher than 800°C are recognizable. This type of curve is very similar to that of Fieldes' allophane A[9]. It is estimated, therefore, that the combination of alumina and silica has proceeded considerably, resulting in the formation of allophane in the specimens of this horizon. Besides the curves of Tc A_{12}~Td A_{11} show endothermic peaks at about 320°C due to the existence of gibbsite or goethite.

(3) The specimens of Ea and Eb show broad endothermic peaks due to the dehydration of water of crystallization, but these peaks shift towards 500°C. Except Ea there are exothermic peaks in the region higher than 800°C. Judging from the form of these curves, the clay fractions of these horizons may be in the stage of transformation of allophane to crystalline hydrated halloysite, or to hydrated halloysite mixed with a small amount of allophane.

(4) The specimens of late Pleistocene, namely those of the deposits lower than $Spfa_1$, show stronger endothermic peaks in the range of 500~600°C. The exothermic peaks in the region higher than 800°C are sharper and moreover these peaks shift towards the higher temperature, hence the crystallization of hydrated halloysite has been proceeded considerably in these horizons.

3. X-ray diffraction analysis

The X-ray powder patterns of all specimens were obtained by a Phillips Geiger counter X-ray spectrometer with Ni filtered Cu Kα radiation or Fe filtered Co Kα radiation. The experimental conditions are as follows: 35 KV, 13 mA, scale factor 4, multiplier 1.0, time constant 4 seconds, scanning speed 2° per minute, angular aperture 1°, receiving slit 0.006 inch.

a) The specimens of Sapporo-Tomakomai lowland district

The X-ray powder diffraction patterns of the specimens from Hayakita, Bibi, Chitose and Shimamatsu are shown in Figs. 5, 6, 7 and 8 respectively. Summarizing the analysis of these patterns, the following results are obtained.

(i) The clay fractions of Ta and Tb horizons show only very weak and broad reflections in the regions of about 10 Å and 3.5 Å, hence these specimens consist of amorphous volcanic glasses not yet crystallized and

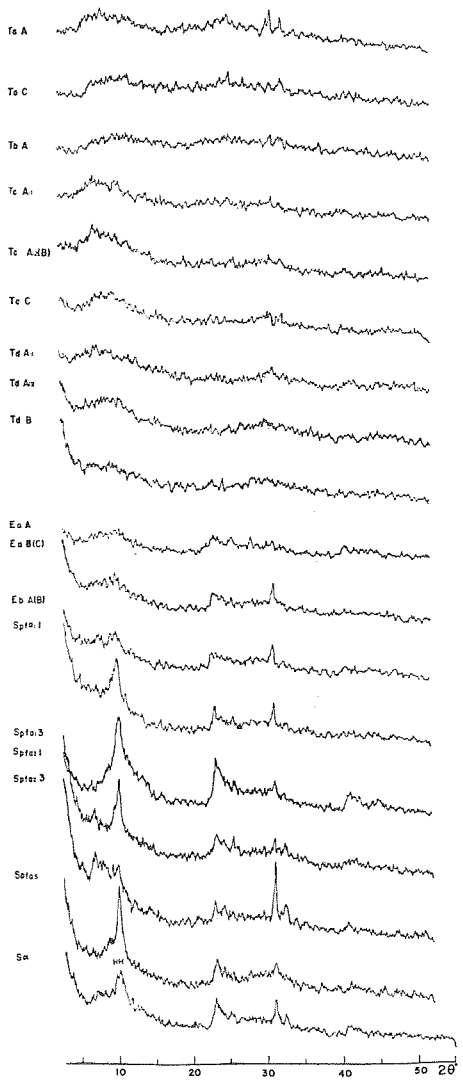

Fig. 5. X-ray diffraction patterns (Hayakita): Co K_α

gel-like substances. This result agrees with that of thermal analysis.

(ii) The patterns of the specimens of Tc and Td horizons of these localities do not show the same tendency, but as the whole the broad reflections of 10 Å and 3.5 Å become clearer than those of Ta and Tb, and the reflections of 3.5 Å of Td are clearer than those of Tc.

(iii) First in the diffraction patterns of the specimens of Ea and

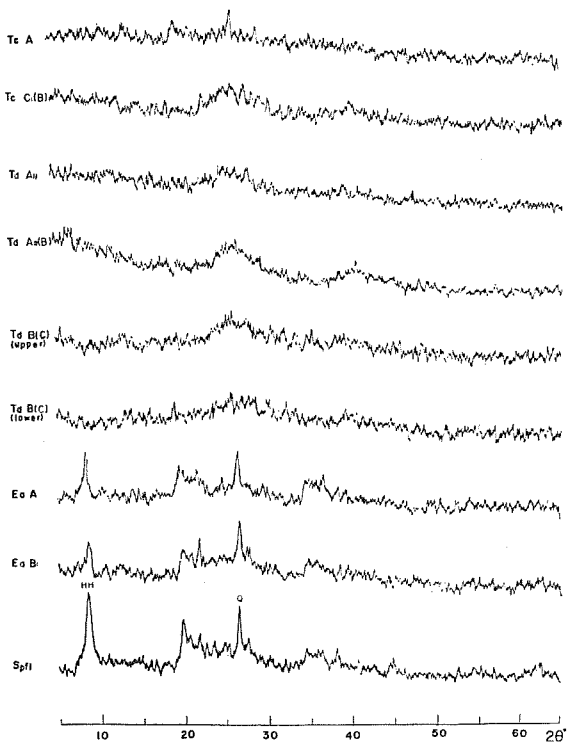

Fig. 6. X-ray diffraction patterns (Bibi): Cu K_α

Eb horizons, the basal reflection of 10 Å is distinct and hence the existence of hydrated halloysite should be estimated. Moreover, there are some specimens, which suggest the existence of irregular mixed layers of halloysite and hydrated halloysite[25,27] (Fig. 7. Eb C_1, C_2, C_3).

(iv) In the diffraction patterns of the specimens of the lower horizons than Spfl, the basal reflection of 10 Å and prismatic reflection of 4.45 Å become clearer and stronger than those of Ea and Eb, hence the crystallization of hydrated halloysite has proceeded remarkably in these horizons.

b) The specimens of the Tokachi district

The X-ray diffraction patterns of the specimens of Shintoku, Obihiro and Kawanishi are shown in Figs. 9, 10 and 11.

The characteristic features of diffraction patterns of these specimens are represented typically by those of Shintoku. Namely the asymmetrical reflections of 4.45 Å, 2.5 Å and the lines of 1.67 Å and 1.48 Å are those of hydrated halloysite, and the line of 3.5 Å due to the halloysite is clear, but their basal reflections are not distinct except the patterns of lowermost

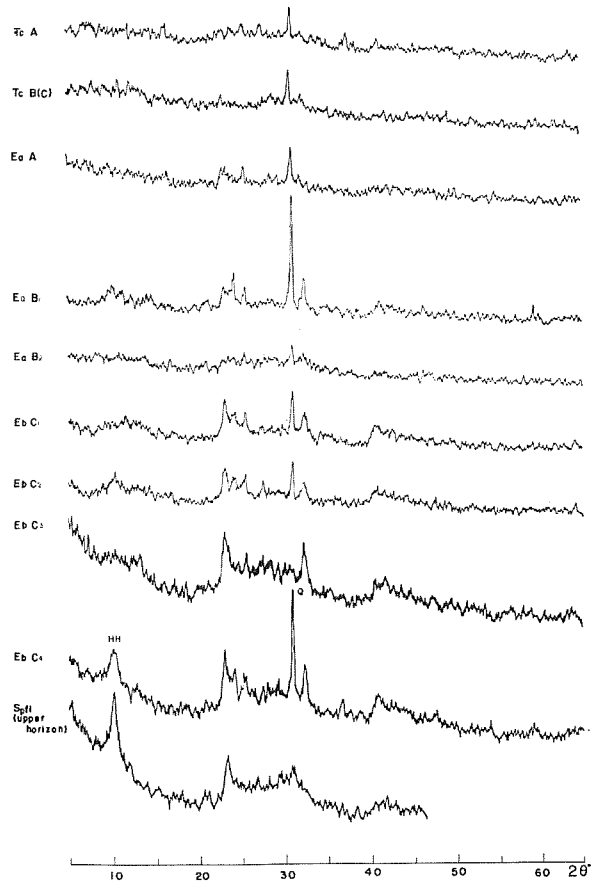

Fig. 7. X-ray diffraction patterns (Chitose): Co K_α

loam, and there exist broad reflections in the range of basal reflections. This type pattern is characteristic of an irregular mixed layer minerals of halloysite and hydrated halloysite. This tendency is already seen in the specimens of To C_1 (700~800 yrs. B.P.) and To C_2 (a few thousands years ago). The remarkable tendency of formation of mixed layer clay minerals in this district may probably due to the fact that these deposits consist of very fine volcanic ashes which are more susceptible to weathering than pumiceous bed.

c) The specimens of Nemuro district

The X-ray diffraction patterns of the clay fractions of the specimens from Nishibetsu of the Nemuro district are shown in Fig. 12. In this district the degree of weathering processes does not always depend on the

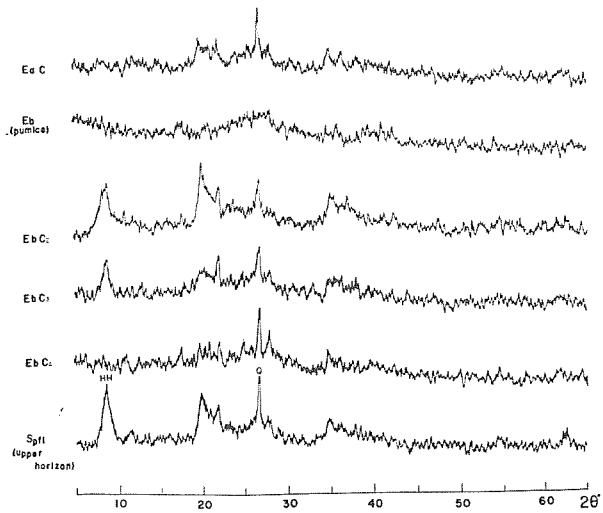

Fig. 8. X-ray diffraction patterns (Shimamatsu): Cu K_α

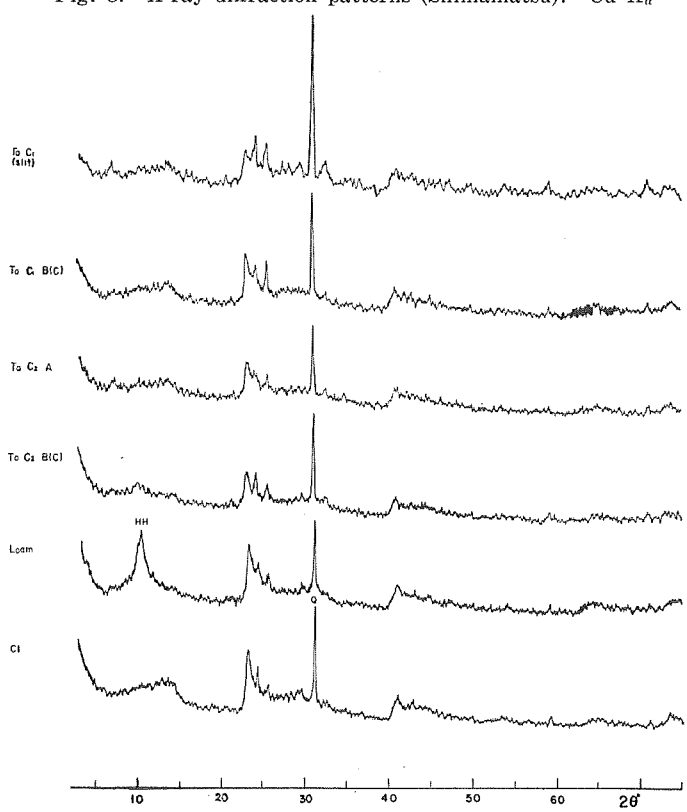

Fig. 9. X-ray diffraction patterns (Shintoku): Co K_α

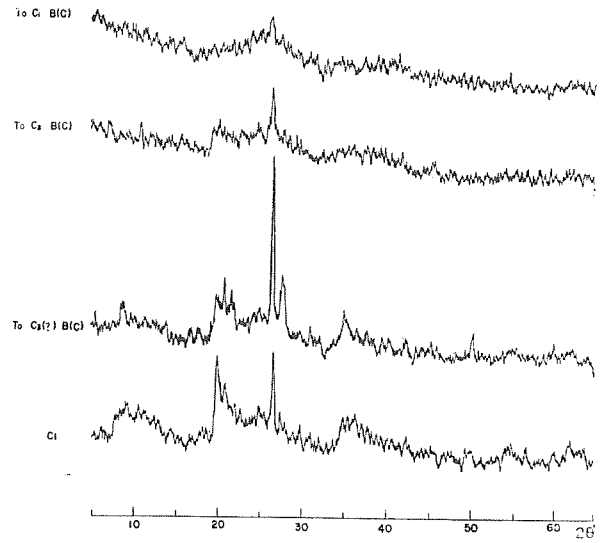

Fig. 10. X-ray diffraction patterns (Obihiro): Cu K_α

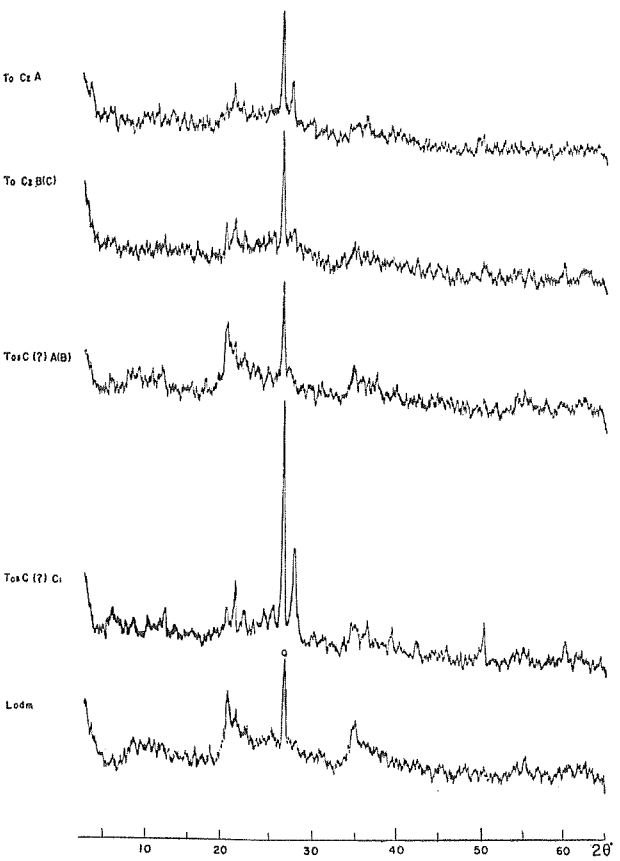

Fig. 11. X-ray diffraction patterns (Kawanishi): Cu K_α

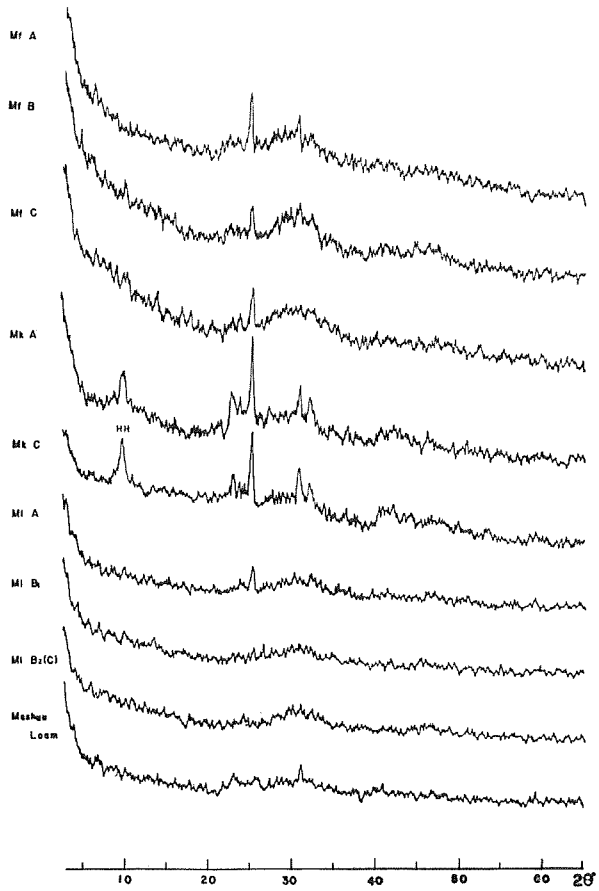

Fig. 12. X-ray diffraction patterns (Nemuro Nishibetsu): Co K_α

length of time. Namely, the specimens of Mk (3,000~5,000 yrs. B.P.) and Ml (more than 5,000 yrs. B.P.) shows only weak broad refrections at about 3.5 Å, which prove the existence of allophane, while the specimens of Mk (more than 5,000 yrs. B.P.), which lies between the above two deposits, show the reflections of 10 Å and 4.45 Å of hydrated halloysite. Ml consists of large grain size pumice. It is concluded from these that duration of weathering on the ground surface and the age are not sufficient to promote the weathering, while Mk, which accumulated on Ml, consists of very fine volcanic ash, so the time interval of Mk exposed on the ground surface was sufficient for the weathering to produce hydrated halloysite.

4. Chemical composition

The chemical analysis was carried out colorimetically for the speci-

mens of Hayakita and Bibi, with the result as shown in Table 5.

The values of SiO_2/Al_2O_3 of Ta and Tb are 3.4 and 3.9 respectively, and resemble the value of 2:1 type clay minerals. But the presence of 2:1 type clay has not been proved in these horizons by the data of differential thermal analysis, X-ray diffraction analysis or infra-red absorption spectra. Hence, these values should show the mean values of gel-like substances and unaltered volcanic glasses of clay fraction. On the other hand, the ratio of SiO_2/Al_2O_3 of Tc and Td is approximately 1, which agrees with that of allophane. In the specimens of Ea, which contains hydrated halloysite of low crystallinity, and those of $Spfa_1$, where hydrated halloysite is predominant, this ratio is about 2, which agrees approximately with the theoretical value of hydrated halloysite.

Table 5. Chemical composition of clay fractions (after K. Goto).

Locality	Hayakita		Bibi		Hayakita	
Horizon	Ta A	Tb	Tc B	Td B	Ea B(C)	$Spfa_1$
SiO_2	27.0	26.9	13.7	17.0	38.0	33.5
Al_2O_3	11.9	13.6	24.8	22.7	31.0	30.3
Fe_2O_3	6.0	6.7	2.8	8.1	10.0	8.0
SiO_2/Al_2O_3	3.9	3.4	0.9	1.3	2.1	1.9

5. Infra-red absorption spectra

Infra-red absorption spectra were recorded on a Hilger H.800 using sodium chloride optices in the region 2,000~650 cm^{-1}. The samples were prepared by using Nujol. The results are shown in Figs. 13~20, and are summarized as follows:

a) The specimens of Sapporo-Tomakomai lowland district

The specimens of the horizons from Ta to Td at Hayakita show asymmetrical weak broad absorption spectra between 850 cm^{-1} and 1250 cm^{-1}, and weak absorptions at 715 cm^{-1} and 800 cm^{-1}, due to the hydrated alumina[1]. In detail, the broad absorption of Ta A-Tc A_{11} has the absorption maximum in the range of 1080~1090 cm^{-1}, while that of Tc A_{12} (B)-Td B shows the absorption maximum at 960~970 cm^{-1}, and as a whole it resembles the absorption spectra of Fieldes' allophane A[8]. The weak absorption at 1300 cm^{-1} (Ta A, Tb A, Td A_{11} and Td B in Fig. 14) may probably be due to the humus which was not eliminated by the treatment of peroxide. In the specimens of lower horizons than Ea, the absorption spectra in the range of 850~1250 cm^{-1} are clearer than those of upper

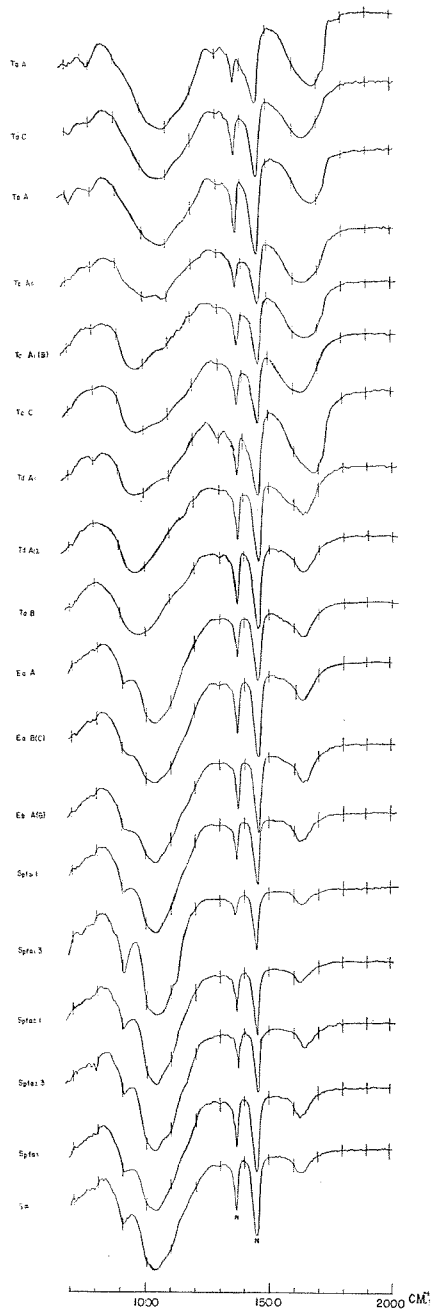

Fig. 13. Infra-red absorption curves (Hayakita)
N: absorption by Nujol

horizons and have the absorption maximum in the neighbourhood of 1040 cm^{-1}, and moreover the absorption due to the vibration of OH radicals

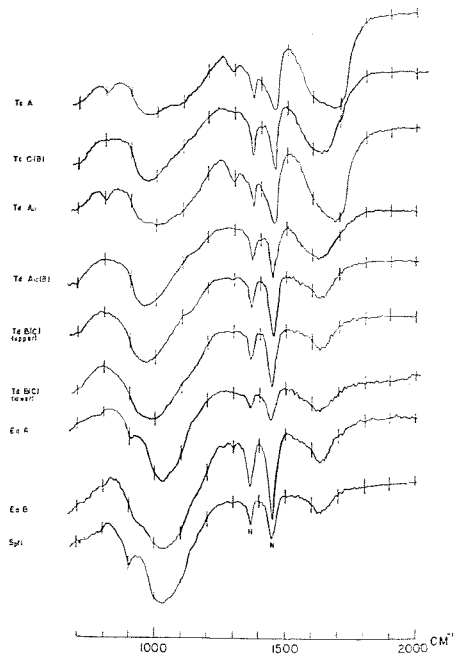

Fig. 14. Infra-red absorption curves (Bibi)

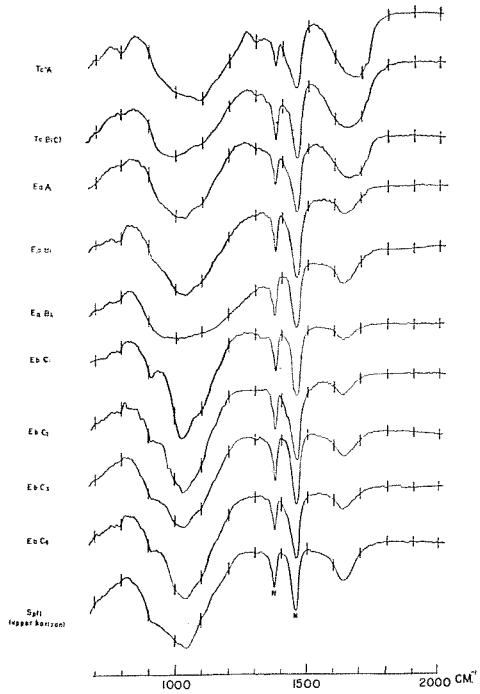

Fig. 15. Infra-red absorption curves (Chitose)

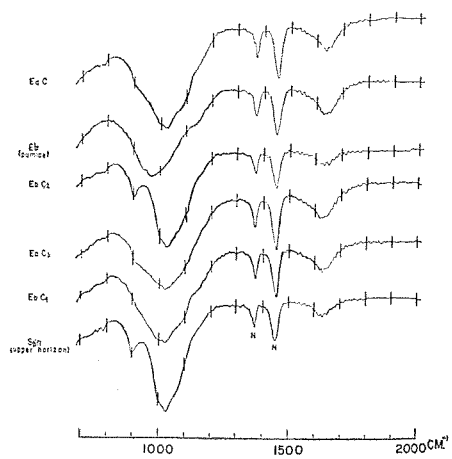

Fig. 16. Infra-red absorption curves (Shimamatsu)

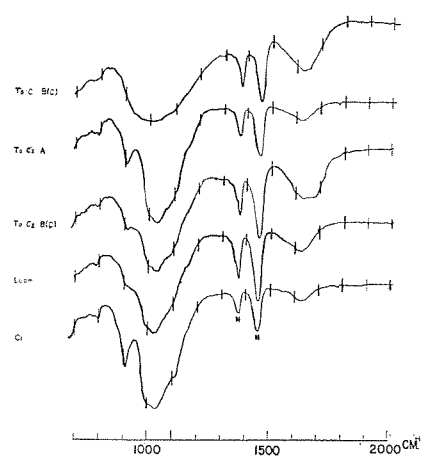

Fig. 17. Infra-red absorption curves (Shintoku)

of kaoline minerals is recognized in the neighbourhood of 910 cm^{-1}. This fact is in good accordance with the result of differential thermal analysis, and X-ray diffraction analysis, which shows that hydrated halloysite was formed at first in the horizons lower than Ea.

The modes of absorption spectra of the specimens of Bibi, Chitose and Shimamatsu (Figs. 14, 15 and 16) are as a whole very similar to those of Hayakita, and the first appearance of the absorption spectra due to hydrated halloysite is noticed in the specimen of Ea also in the specimens from these localities.

b) The specimens from the Tokachi district

The infra-red absorption spectra of the specimens of Tokachi district are shown in Figs. 17, 18 and 19, and the mode of their absorption spectra is shown typically by that of Shintoku. The absorption spectra of To C_1 (B)C show the broad absorption band having a maximum at 1015 cm^{-1}, and resemble those of allophane A. The specimens of the horizons lower than To C_2 show the absorption spectra in the range of 905~910 cm^{-1}, and a broad absorption band having a maximum at about 1030 cm^{-1}. These feature resemble those of specimens of the horizons lower than Spfl in the Sapporo-Tomakomai lowland district. It may be recognized from the figures as a whole that the degree of crystallization of the specimens increases from the upper horizon to the lower. This tendency is also recognized in the specimens at Obihiro and Kawanishi. The infra-red absorption spectra of To C_1 B(C) at Obihiro show only asymmetrical

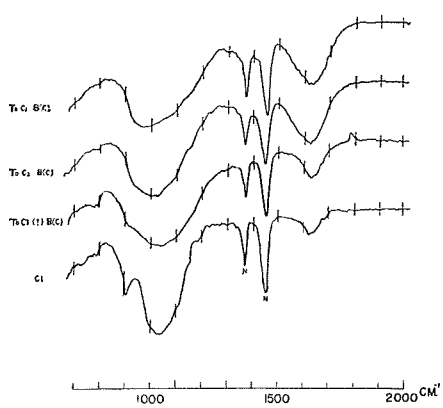

Fig. 18. Infra-red absorption curves (Obihiro)

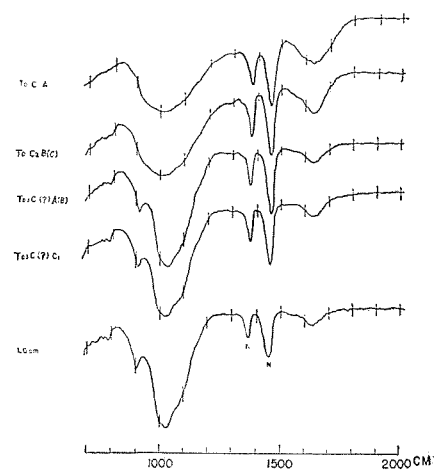

Fig. 19. Infra-red absorption curves (Kawanishi)

broad absorption band having a maximum at about 950 cm^{-1}, while those of the specimens lower than To C_2 become symmetrical and can be divided into the absorptions at 910 cm^{-1} and 1040 cm^{-1}. The specimens of To C_1 A and To C_2 B(C) at Kawanishi show the broad absorption band, but those of the lower horizons than To C_3 A(B) show the absorption band inherent to hydrated halloysite.

c) The specimens of the Nemuro district

The infra-red absorption spectra of the specimens of Nemuro district are shown in Fig. 20. The specimen of Mf A shows a broad absorption

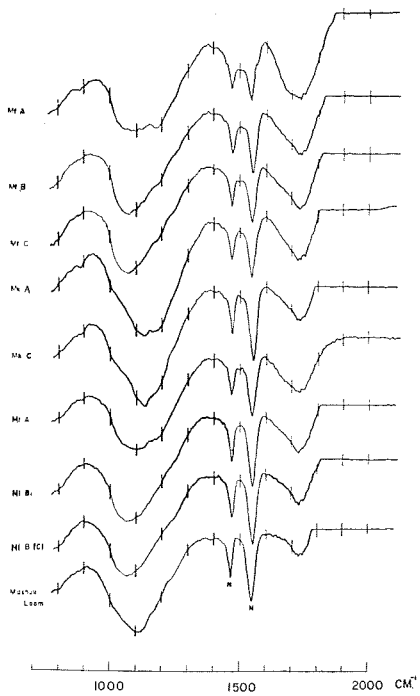

Fig. 20. Infra-red absorption curves (Nemuro Nishibetsu)

band, and the spectra of Mf B and Mf C resemble those of allopane A. The patterns of Mk A and Mf C show the absorption band having a break at about 900 cm^{-1} and the absorption maximum at 1030 cm^{-1}. But the absorption spectra of the specimens of Ml horizon, lower than Mk, show a broad absorption resembling that of allophane A, and the lowest specimen, namely the Mashu loam shows the pattern resembling that of Mk horizon, or that of hydrated halloysite.

The results of infra-red absorption spectra as above mentioned are

in good accordance with the data obtained by either differential thermal analysis, or X-ray diffraction analysis.

6. Electron micrographs

The examination by an electron microscope was carried out mainly on the specimens of Sapporo-Tomakomai lowland district. The electron micrographs of these specimens were taken by a Hitachi HS-6 type electron microscope. The preparation of these specimens for this experiment was as follows: After the specimens were dispersed on collodion membrane by the technique of water-paste method, they were shadowed by chromium and strengthened by carbon evaporation.

The results of the observation by the electron microscope are as follows:

Mainly such flakes with irregular but well-defined outlines, and the assemblages of very fine particles (0.02 μ) are observed in the electron micrographs of the specimens of Ta and Tb. The former may probably be the fragments of non-altered volcanic glasses, and the latter gel-like materials (Pl. 1-1, -2). But these fragments are very scanty in the specimens of Tc and Td, while the assemblages of very fine particles (0.05 μ) are observed (Pl. 2-3, -4). Judging from the data of thermal analysis, X-ray analysis and infra-red absorption, these assemblages may be allophane A. Moreover there exist bundles of laths, in some specimens of these horizons, especially in such specimens which show the endothermic reaction in the thermal analysis at about 320°C (Fig. 4). It is inferred from these facts that these bundles may be minute crystals of goethite or gibbsite.

Chaff-shaped particles of the dimention 0.2×0.1 μ, and kale-shaped, or rounded grains having concentric plaits are observed in the specimens of Ea and $Spfa_1$ (Pl. 3-5, -6). It has been usually accepted that the electron micrograph of halloysite minerals shows tubular partices. The specimens now under consideration are in the stage of hydrated halloysite of low degree of crystallinity with a small amount of remaining allophane. Therefore these peculiar particles may be interpreted as the shape of hydrated halloysite in the lower degree of crystallization.

IV. Summary and conclusion

The writer has made systematic studies on the clay fractions of the altered products of many pyroclastic deposits and volcanic ashes of late Pleistocene to Recent from eight localities in southern Hokkaido. The

problem of weathering of these deposits was investigated clay mineralogically by means of several manipulations as described above. The results obtained are summarized as follows:

1. Samples of the Sapporo-Tomakomai lowland district

a) Volcanic glasses are not yet altered to allophane in the upper horizons, namely in the specimens of Tarumai *a* pumice-fall deposit and Tarumai *b* pumice-fall deposit (less than 3000 yrs. B.P.). It seems that gel-like substances and non-altered glass fragments are the dominant components in these clay fractions.

b) Allophane A described by Fieldes is formed in Tarumai *c* pumice-fall deposit (800~900 yrs. B.P.), and Tarumai *d* pumice-fall deposit (3,000~5,000 yrs. B.P.) and weathering process is more advanced in the latter than in the former and hydrated halloysite of the low degree of crystallization appears first in Eniwa *a* and *b* pumice-fall deposits (more than 5,000 yrs. B.P.).

c) Hydrated halloysite is predominated in the late Pleistocene deposits, namely in the Shikotsu pumice-flow and Shikotsu pumice-fall deposit (20,000 yrs. B.P.).

2. Samples of the Tokachi district

The samples of this district are characterized by the appearance of an irregular mixed layer of halloysite and hydrated halloysite. The mixed layer type is already recognizable in Tokachi C_1 volcanic ash deposit (700~800 yrs. B.P.) at Shitoku, but generally speaking, the upper horizon is rich in allophane, while an irregular mixed layer of halloysite and hydrated halloysite is predominant in Tokachi C_2 ash deposit (more than a few thousands years B.P.).

3. Samples of the Nemuro district

Exceptional irregularity of alteration of allophane to hydrated halloysite is noticed in these specimens. Namely the dominant clay mineral is allophane, in the upper Mashu *f* pumice-flow deposit (3,000~5,000 yrs. B.P.), while hydrated halloysite is dominant in Mashu *k* ash deposit, and again allophane is predominant in the lower Mashu *l* pumice-fall deposit (more than 5,000 yrs. B.P.). This fact seems to suggest that an alteration process of allophane to hydrated halloysite is determined not only by the time factor, but is also influenced by the length of the weathering of the deposits at the ground surface, and by the size of particles of the parent materials.

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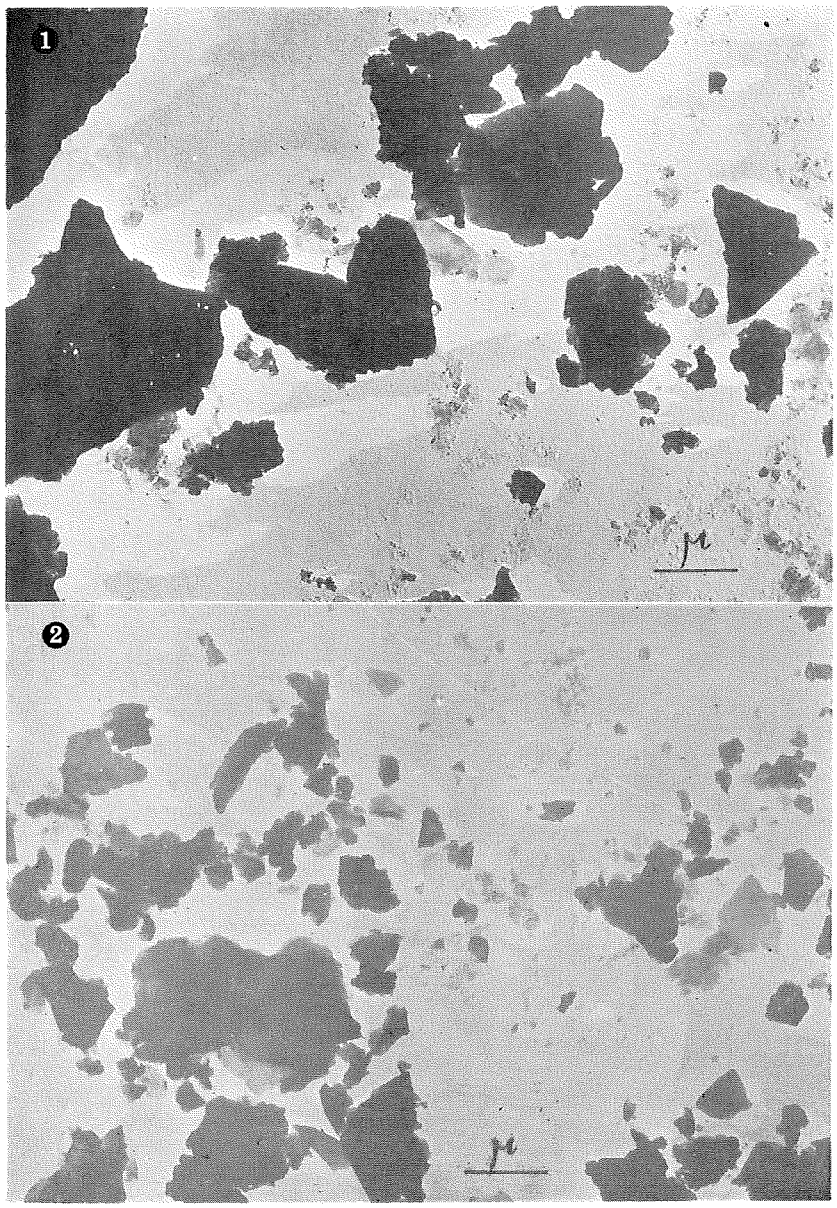
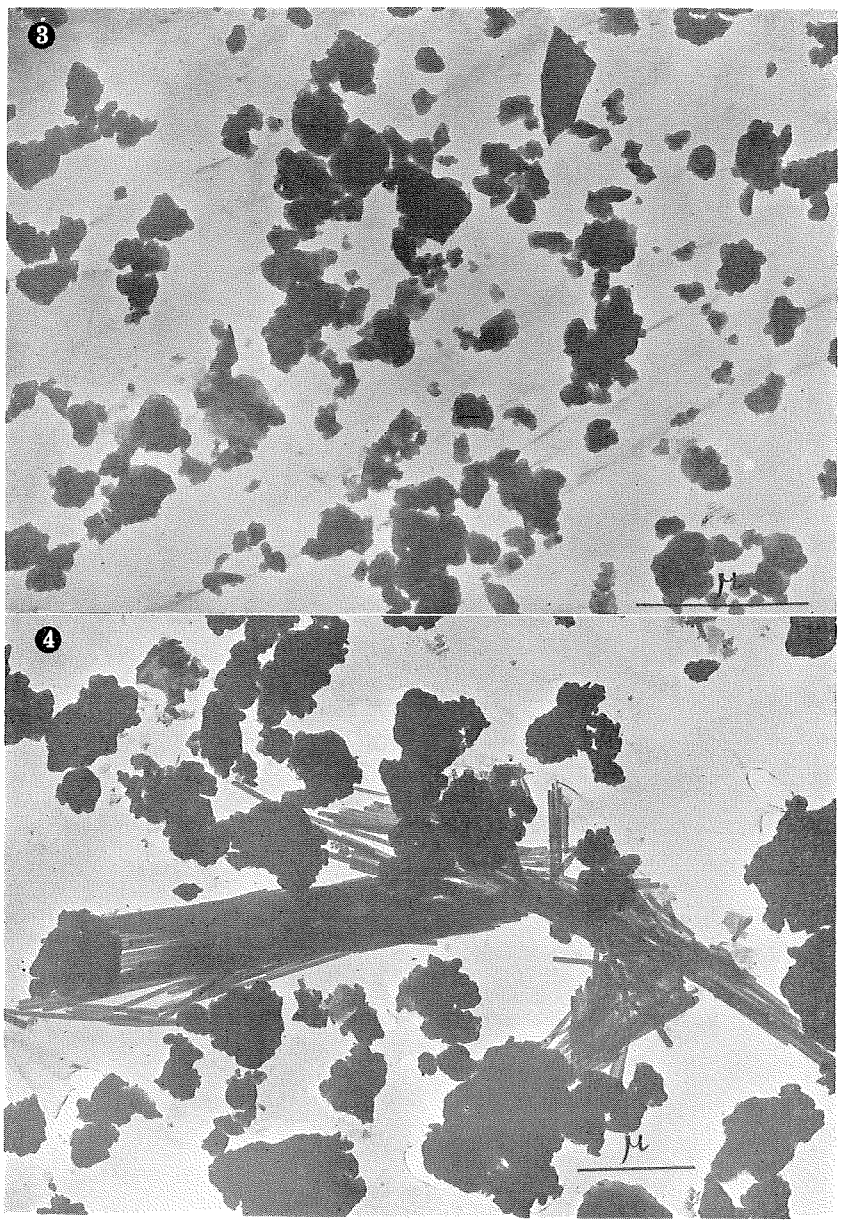
References

1) BEUTELSPACHER, H., (1956); Infrarot-Untersuchungen an Bodenkolloiden. VI Congres International de la Science du sol. B, 329-336.
2) DOI, S., (1953); Explanatory text of the geological map of Shiraoi. Scale 1: 50,000. Geological survey of Hokkaido.
3) DOI, S., and OSANAI, H., (1953); Explanatory text of geological map of Ishiyama. Scale 1:50,000. Geological survey of Hokkaido.
4) DOI, S., and OSANAI, H., (1955); The welded tuffs of Hokkaido. Earth Science (Chikyu Kagaku)., No. 23, 1-6.
5) DOI, S., and OSANAI, H., (1956); On the so-called Shikotsu-welded tuff. Jour. Geolg. Soc. Japan, **62**, 1-6.
6) DOI, S., (1957); Explanatory text of the geological map of Tarumai. Scale 1:50,000. Geological survay of Hokkaido.
7) FIELDES, M., (1955); Clay mineralogy of New Zealand soils. Part 2. Allophane and related mineral colloids., New Zealand Jour. Sci. Tech., **37**, 336-350.
8) FIELDES, M., WALKER, I. K., and WILLIAMS, P. P., (1956); Clay mineralogy of New Zealand soils. Part 3. Infra-red absorption spectra of soil clays. New Zealand Jour, Sci. Tech., **38**, Section B, 31-43.
9) FIELDES, M., (1957); Clay mineralogy of New Zealand soils, Part 4. Differential thermal analysis., New Zealand Jour. Sci. Tech., **38**, Section B, 533-570.
10) ISHII, J., and MORI, T., (1959); Studies on the clay in volcanic ash soil in Ishiyama, near Sapporo. Jour. Geol. Soc. Japan, **65**, 357-363.
11) ISHII, J., and SASAKI, T., (1959); Studies on the clay in clayey loam in the southern part of Tokachi Province, Hokkaido. Bull. Geol. Comm, Hokkaido, No. 38, 13-21.
12) ISHIKAWA, T., and MINATO, M., (1953); Geological age of welded tuff in Northern Japan. Acta. INQUA, No. 4, 1~2.
13) KATSUI, Y., (1958); On the fossil forest embeded in Shikotsu pumice-fall deposit. Jour. Geolog. Soc. Japan, **64**, 379-385.
14) KATSUI, Y., (1959); Chemical composition of the lavas from Quaternary volcanoes of

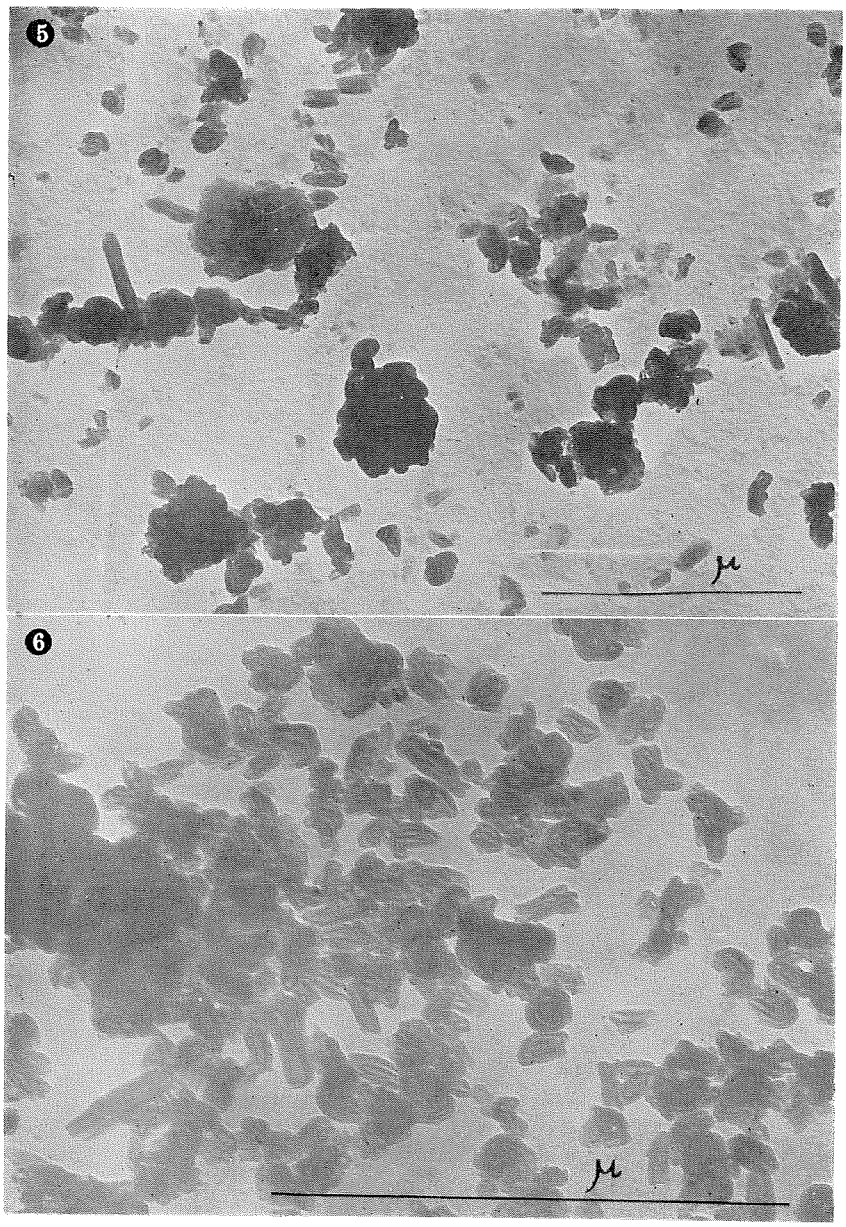
Hokkaido. Bull. Geol. Comm. Hokkaido, No. 38, 27–47.
15) KATSUI, Y., (1959); On the Shikotsu pumice-fall deposit with special reference to the activity just before the depression of the Shikotsu Caldera. Bull. Volcan. Soc. Japan, **4**, 33–48.
16) MACKENZIE, R. C., and MELDAU, R., (1959); The aging of sesquioxide gels. I. Iron oxide gels. Min. Mag., **32**, 153–165.
17) MATSUI, T., (1960); On clay minerals in recent soil and palaeosoil derived from the Pleistocene volcanic ash near Utsunomiya. Abstract of advances in clay sience (2). Clay research group of Japan. 229–241.
18) MINATO, M. and HASHIMOTO, S., (1954); Zur zwei Eiszeiten im Hidaka-Gebirge, Hokkaido, Japan. Jour. Geol. Soc. Japan, **60**, 460.
19) MINATO, M. and HASHIMOTO, S., (1954); Zur Karlbildung im Hidaka-Gebirge Hokkaido Japan. Proc. Japan. Acad., **30**, 106–108.
20) MINATO, M., (1955); The outline of the Quaternary Geology in Hokkaido (in Japanese). Kagaku (Science), Iwanami **25**, 108–116.
21) MINATO, M., and HASEGAWA, Y., (1959); Studies on the welded tuffs in Japan, 1st report. On the Neppu welded tuff. Jour. Geol. Soc. Japan, **65**, 66–70.
22) MINATO, M., ISHII, J., and KUMANO, S., (1959); Studies on the welded tuffs in Japan 2nd report. On the Shikotsu welded tuffs. Jour. Geol. Soc. Japan. **65**, 209–221.
23) SASAKI, S., and ISHIZUKA, Y., (1957); On the volcanic ash soil in Tokachi district, Hokkaido, Japan. Soil and Plant Food, **2**, 177–183.
24) SEO, H., (1951); 1st report of the pedological studies of Hokkaido National Agricultural Experiment Station.
25) SUDO, T., (1956); X-ray and thermal data for clay minerals formed by the alternation of volcanic meterial, Sci. Rep. Tokyo Kyoiku Daigaku, Section C. **43**, 39–55.
26) SUDO, T., (1953); Particle shape of a certain clay of hydrated halloysite as revealed by the electron micrograph. Miner. Jour., **1**, 66–68.
27) TSUCHIYA, T., and KURABAYASHI, S., (1958); On the clay minerals of the Kanto loam. Jour. Geol. Soc. Japan, **64**, 605–615.
28) URAGAMI, K., YAMADA, S., and NAGANUMA, Y., (1933); Studies on the volcanic ashes in Hokkaido. 1st report. Bull. Volcan. Soc. Japan, **1**, 44–60.
29) URAGAMI, K., NAGANUMA, Y., and TOGASHI, R., (1933); Studies on the volcanic ashes in Hokkaido. 2nd report. Bull. Volcan. Soc. Japan, **1**, 81–94.
30) YAMADA, S., (1958); Studies on the history of volcanic eruption of Alluvium Epoch in Hokkaido on the basis of depositonal features of the pyroclastics. Association of the Geological Collaboration Monograph, No. 8. pp. 40.



Electron micrograph (1) Ta A (2) Tb A
See p. 566 for explanation.



Electron micrograph (3) Tc C (4) Td A
See p. 566 for explanation.



Electron micrograph (5) Ea A (6) $Spfa_1$
See p. 566 for explanation.