

Weathering Processes of the Quaternary pyroclastic Deposits of the Usu Volcanic District, Hokkaido

By

Yūkō KONDŌ

(Laboratory of Soil and Fertilizer, Obihiro Zootechnical
University, Obihiro, Hokkaido, Japan)

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北海道有珠火山地域における第四紀火山碎屑物の風化過程

近 堂 祐 弘*

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CHAPTER 1. INTRODUCTION

Since the dawn of this century, rock weathering process has been studied by geologists, mineralogists, geochemists, and soil scientists. Three principal ways for the study of rock weathering process have been introduced.

As a chemical investigation proceeded, the weathering process has been considered by comparing a chemical composition of fresh parent rock with that of the weathered rock, the difference being attributed to gains or losses of chemical elements with respect to a supposed immobile elements, usually aluminum (HARRISON, 1933; POLYNOV, 1937; KELLER, 1957, p. 45-48).

* 帯広畜産大学土壌肥科学研究室

The second aspect is a mineralogical one, in which interests are directed toward skeletal minerals surviving against severe attacks of weathering. On the basis of these observations, the sequence of resistibility or stability to weathering can be determined for many rock-forming minerals (GOLDICH, 1938). However investigators have not always agreed on such step-by-step mechanism by which one mineral is weathered or altered to another. During last twenty years, the third aspect, clay mineralogical study, has been developed. Primary rock-forming minerals are weathered into very fine-grained materials most of which have been believed to be amorphous until techniques now used in clay mineralogical research proved their crystalline state. Besides primary relict minerals, weathered materials are now known to consist of both amorphous and crystalline secondary minerals, mostly appearing in $<2 \mu$ fraction and being objects of interest in clay mineralogy.

Any study of rock weathering process hitherto performed stood on the three aspects above mentioned. Most of the studies, however, seem to fall into the common tendency of dealing with materials as bulk mass. That is, those concern much more with fresh rocks versus their weathered end products as a whole, rather than with the process or mechanism by which fresh rocks changed into weathered materials. For example, in the subtropical or tropical humid region, it is well known that, kaolinite minerals, bauxite (gibbsite, boehmite, goethite, and diaspore) and some of 2:1 type clay minerals are found in deep weathered rocks and deposits. However, an intermediate process through which the above clay minerals were derived from the constituent minerals of the parent rocks or deposits, is scarcely understood. The problem of rock weathering will be revealed by investigation of weathering process especially its initial phase.

A vivid initial phase of the weathering process, may be provided in the temperate to subarctic humid region. For this reason, a study of weathering of pyroclastic rocks in Hokkaido, north Japan, will offer an important contribution to this problem.

Hokkaido island has been a site of intense volcanic activity during Quaternary period through which some 50 volcanoes have erupted along the inner zones of the Kurile and the Honshû arcs. A number of the Quaternary pyroclastic deposit are widely distributed in this island, especially the pumice-fall and -flow deposits cover ca. 53% of this island, commonly intercalating buried soils among them (Figs. 19 and 20). Tephrochronological studies on these pyroclastic deposits have been carried on by not a few pedologists, geologists, and archaeologists, since 1933. Little attention, however, has been paid to the weathering process of these pyroclastic deposits from a view point of mineralogy. Recently, ISHII and the present writer endeavored to identify the clay minerals found in the weathered products from these pyroclastic deposits of felsic andesitic—rhyolitic characters, and to elucidate crystallization process of volcanic glasses during the weathering (ISHII and KONDÔ, 1962 a, b). According to them the pumice- and ash-fall deposits rich in felsic glass seem to undergo, in the course of the time, the following

weathering process :

Volcanic glass (felsic)→allophane A→halloysite→mixed-layer mineral of halloysite-metahalloysite→metahalloysite.

A similar conclusion was also reached by the studies on weathering of the Quaternary pyroclastic deposits in Japan (e.g., SUDŌ, 1959; TSUCHIYA and KURAHAYASHI, 1958, 1959; KANNO, 1959, 1961 b; AOMINE and WADA, 1962; MATSUI, 1960; KURAHAYASHI and TSUCHIYA, 1965), and the pyroclastic deposits in New Zealand (FIELDES and SWINDALE, 1954; FIELDES, 1955 a, b), Hawaii (BATES, 1962), and Chile (BESOAIN, 1964).

An implicit assumption in these studies is that the weathering of pyroclastic deposits increases with depth, which implies a measure of the weathering time after deposition. This might be correct at a megascopic order, but effects by other factors apt to be overshadowed. At this stage, a study of the other factors of weathering is also demanded for the further detailed research. Materials for such study seem to be provided in the Usu volcanic district, Hokkaido.

The Usu volcanic district is located in the southwestern part of Hokkaido, and occupies the northern end of the Nasu volcanic zone. In this district, a great deal of pyroclastic deposits ranging from late Pleistocene to Holocene are widely developed. Distribution, source, age and mode of emplacement of these deposits have been studied in detail from a tephrochronological view point (YAMADA, 1958; KONDŌ, 1962, 1963; YAMADA *et al.*, 1963; ÔBA and KONDŌ, 1964; ÔBA, 1966; MINATO, 1966).

Petrographic character of these pyroclastic deposits changes from basalt to rhyolite. Accordingly, an interesting problem that different modes of weathering process may be shown due to difference in chemical and mineralogical compositions of the parent materials, will be also discussed in this work. Furthermore, weathering of pyroclastic materials takes place not only after their deposition. Some of the materials may have already weathered prior to their eruption. Such consideration will be paid on the pyroclastic deposits in the Usu district.

CHAPTER 2. OCCURRENCE OF THE PYROCLASTIC DEPOSITS

Geologic map, columnar sections and geologic succession of the pyroclastic deposits of this district are shown in Figs. 1 and 2, and Table 1. Quaternary pyroclastic deposits and the history of the Usu volcano are concerned here.

Basement rocks: Tertiary formations constituting the basement of the volcano, are composed of altered volcanic rocks and pyroclastic deposits of Miocene, and pumice-flow deposits (partly welded) and lavas of Pleiocene (ÔTA, 1956).

Miocene pyroclastic deposits are generally suffered from hydrothermal alteration. Ore deposits of iron sulphide are found in these deposits. Well-crystallized kaolinite occurs in the altered plagio-rhyolitic tuff-breccia near the iron sulphide ore deposit (Plate V, Fig. 2). These basement materials are considerably eroded

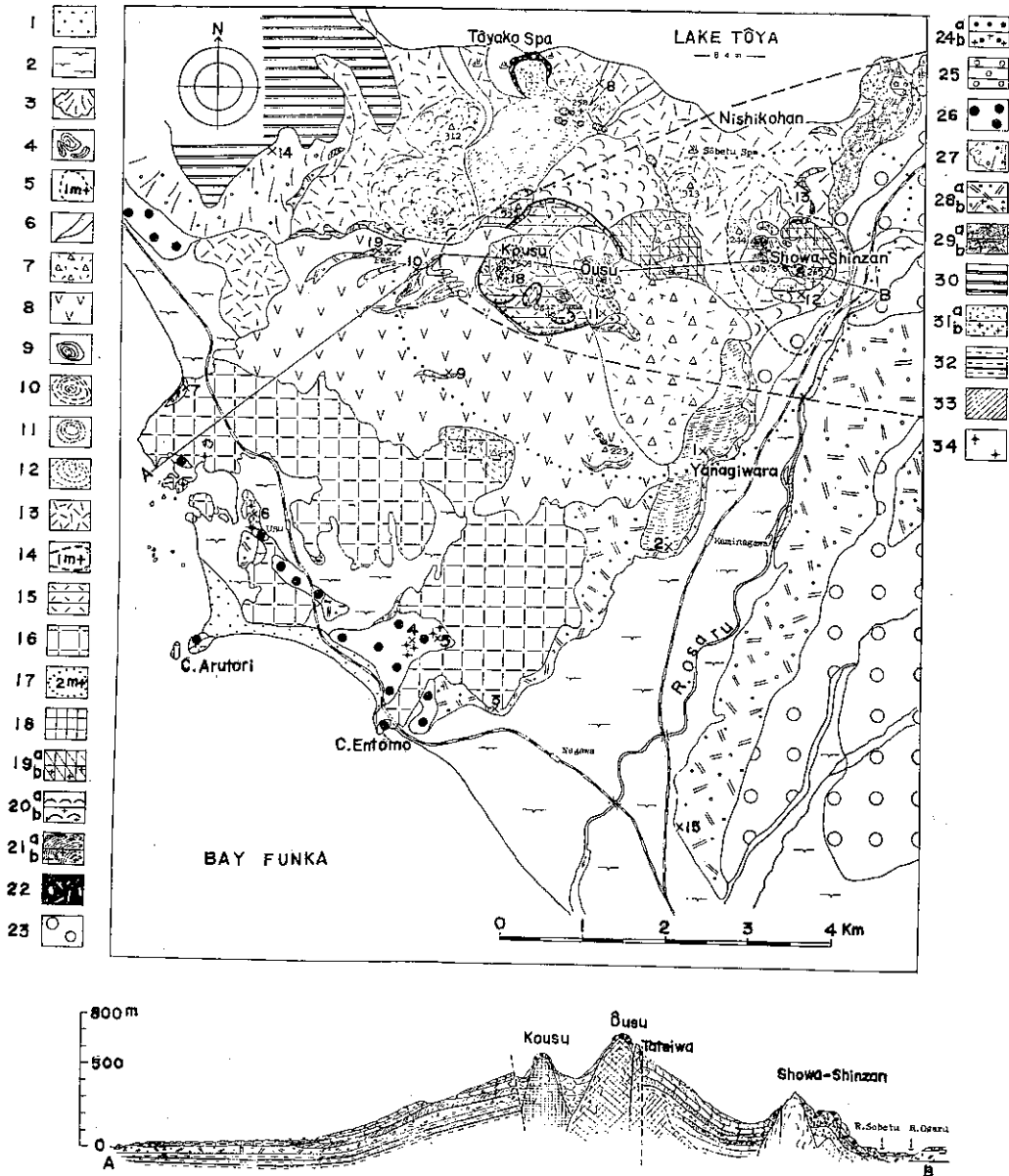


Fig. 1. Geological map of Volcano Usu.

Explanation of the Geological Map.

- | | | |
|--|---|---|
| Erosion products
(Holocene) | { | <ul style="list-style-type: none"> 1. Sand dune deposits. 2. Alluvium. 3. Talus deposits. |
| Products from the
parasitic craters of
the volcano Usu
(Holocene) | { | <ul style="list-style-type: none"> 4. New lava of Shōwa-Shinzan (hypersthene-dacite). 5. Ejecta of Shōwa-Shinzan (distribution of ejecta, 1m in thickness.) 6. Yosomiyama mud-flow deposits. |

- | | | |
|--|---|--|
| Products from the volcano Usu (Holocene) | { | 7. Tateiwa pyroclastic flow (dacitic lava block). |
| | | 8. Bunsei pyroclastic flow (dacitic lava block and pumice). |
| | | 9. Ogariyama dome lava (hypersthene-dacite). |
| | | 10. Ô-usu dome lava (hypersthene-dacite). |
| | | 11. Ko-usu dome lava (hypersthene-dacite). |
| | | 12. Crypto domes. |
| | | 13. Usu a ₃ mud-flow deposits (montmorillonite clay and andesitic ash). |
| | | 14. Usu b pumice-fall deposits (rhyolitic pumice). |
| | | 15. Atrio-deposits (montmorillonite clay, sand and gravel). |
| | | 16. Zenkôzi mud-flow deposits (augite-hypersthene-andesitic lava block). |
| | | 17. Somma scoria-fall and -flow deposits (distribution of scoria, 2 m in thickness). |
| | | 18. Mt. 554 m lava (augite-hypersthene-andesite). |
| | | 19. a) The 4th somma lava (pigeonite-hypersthene-andesite). |
| | | b) (The part broken to block by elevation). |
| | | 20. a) The 3rd somma lava (augite-hypersthene-andesite). |
| | | b) (The part broken to block by elevation). |
| | | 21. a) The 2nd somma lava (olivine-augite-hypersthene-basalt). |
| | | b) (The part broken to block by elevation). |
| | | 22. The 1st somma lava (augite-hypersthene-olivine-basalt). |
| Erosion products (Holocene) | { | 23. The 2nd river terrace deposits. |
| Erosion products (upper Pleistocene) | { | 24. a) The 1st river terrace deposits. |
| | | b) (The red coloured part by heating with dome lava). |
| | | 25. Lake deposits. |
| | | 26. Marine terrace deposits. |
| | | 27. Horomoe creeping deposits. |
| Products from the volcano Tôya (upper Pleistocene) | { | 28. a) Tôya pumice-flow deposits (rhyolitic pumice and ash). |
| | | b) (The red coloured part by heating with dome lava). |
| Basement rocks (Pliocene) | { | 29. a) Takinoue welded tuff (hypersthene-augite-dacite). |
| | | b) (The part broken to block by elevation). |
| | | 30. Nottoko lava (hypersthene-augite-andesite). |
| | | 31. a) Sôbetsu pumice-flow deposits (dacitic pumice and ash). |
| | | b) (The part broken to block by elevation). |
| Basement rocks (Osaru-gawa formation, Miocene) | { | 32. Plagio-rhyolitic tuff-breccia. |
| | | 33. Greyish black mudstone. |
| | | 34. Pre-historic sites (shell beds of Jômon and post-Jômon stage). |

and covered by the younger volcanic materials and terrace deposits.

The late Pleistocene formations, building also the basement of the volcano, are thick pumice-flow deposits, pumice-fall and terrace deposits.

Tôya pumice-flow deposits: Voluminous pumice-flows were intermittently erupted during the late Pleistocene, resulting in formation of the Tôya caldera of Krakatau type. In this district, two pumice-flow deposits are distributed: Tôya pumice-flow 1 (Tpfl₁) and Tôya pumice-flow 2 (Tpfl₂), as shown in Table 1 and Fig. 2. Dating on the carbonized wood trunk discovered from the lower most horizon of the Tôya pumice-flow 2 (Tpfl₂) procures an age of 13900 ± 250 yrs. B.P. (G&K-521) (MINATO, 1966).

The Tôya pumice-flow deposits are mainly composed of light pink volcanic

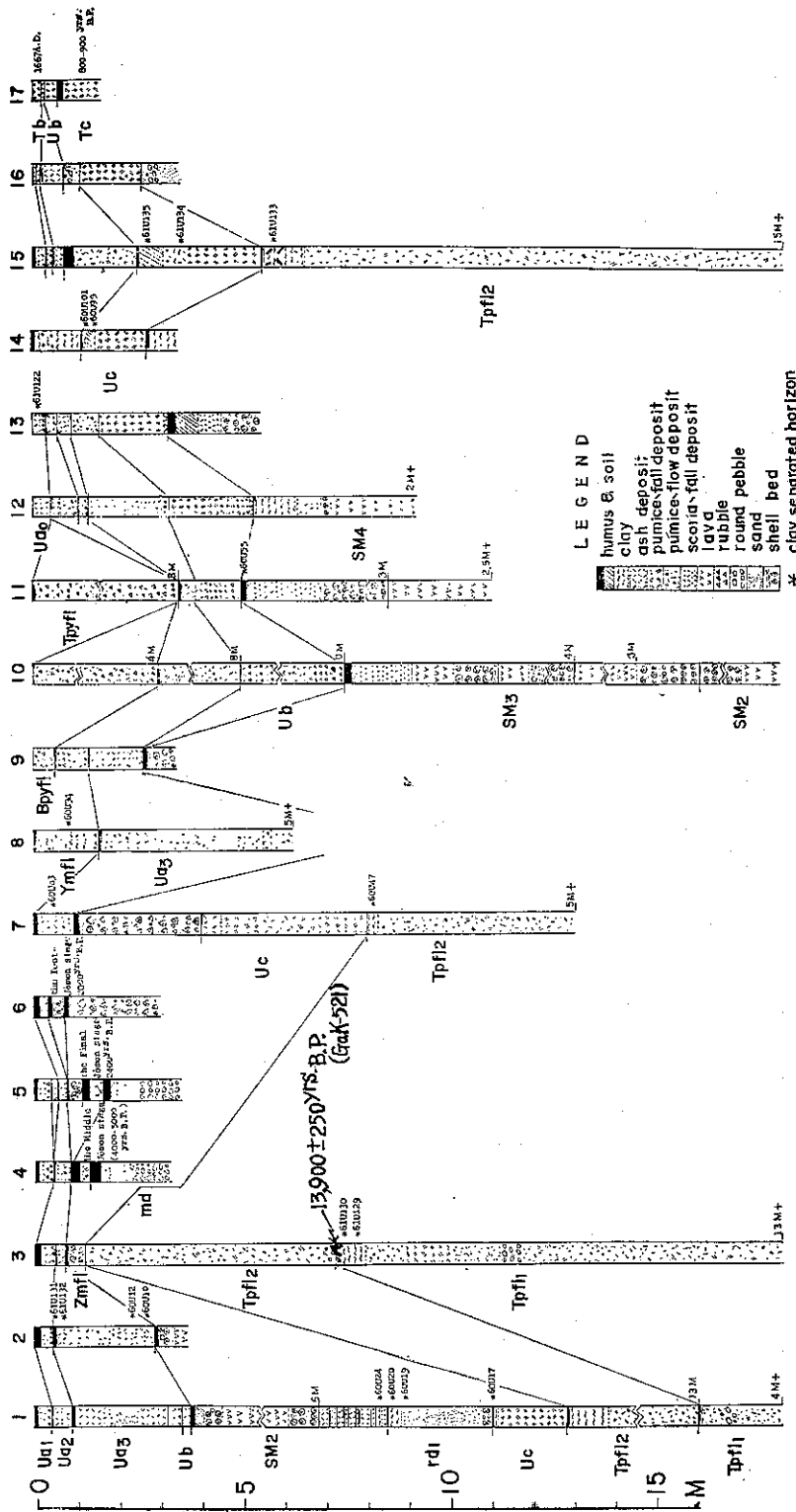


Fig. 2. Columnar sections of the pyroclastic deposits in the environs of the Volcano Usu.

Number of each column is plotted in Fig. 1.

U₄₀: Shōwa-Shinzan ash-fall Ymfl: Yosomiyama mud-flow Tpyfl: Tatewa pyroclastic flow Bpyfl: Bunsai pyroclastic flow U₄₁: Usu a₁ ash-fall U₄₂: Usu a₂ ash-fall U₄₃: Usu a₃ ash-fall & mud-flow U_b: Usu b pumice-fall Zmfl: Zenkozi mud-flow SM₄: The 4th somma lava SM₃: The 3rd somma lava SM₂: The 2nd somma lava U_c: Usu c pumice-fall (erupted from the Volcano Nakajima) Tpf₂: Toya pumice-flow 2 Tpf₁: Toya pumice-flow 1 Tb: Tarumai b pumice-fall Tc: Tarumai c pumice-fall md: Marine terrace deposits rd₁: The 1st river terrace deposits

Table 1. Geological succession of the basement formations and the pyroclastic deposits of Usu volcano (after KONDÔ, 1963; ÔBA, 1966)

Age	Erupting materials of Usu volcano		Other deposits	Remarks (volcanic activities)		
	Stage	Lavas			Pyroclastics	
Quaternary	Holocene	Final stage (domes and pyroclastics)	Dome lava of Shôwa-Shinzan	Shôwa-Shinzan ash-fall (Ua ₀) Yosomiyama mud-flow deposit Tateiwa nuée ardente deposit Bunsei nuée ardente deposit "Ua ₁ " ash-fall deposit "Ua ₂ " ash-fall deposit "Ua ₃ " ash-fall & mud-flow deposit "Ub" pumice-fall deposit	Fluvial deposit Talus deposit	Shôwa-Shinzan Ua ₀ (1943-1945) Yosomiyama (1910) Tateiwa nuée ardente (1853) Bunsei nuée ardente (1822) Ua ₁ (1882 or 1768) Ua ₂ (1663) Ua ₃ (350-500 yrs. B.P.) Ub pumice-fall (350-500 yrs. B.P.)
			Dome lava of Ô-Usu		Atrio deposit	Crater of the summit (2000-2400 yrs. B.P.)
			Dome lava of Ko-Usu	Zenkôji mud-flow deposit		
			The 4th somma lava The 3rd somma lava The 2nd somma lava The 1st somma lava	Scoria-flow deposit (each lavas accompanying scoria-fall deposit)		Formation of a strato-cone
Pleistocene	Basement	The 1st river terrace deposit Lower marine terrace deposit "Uc" pumice-fall deposit (erupted from the Nakajima volcano) Tôya pumice-flow deposit 2 (Tp _{h2}) Tôya pumice-flow deposit 1 (Tp _{h1})		Nakajima volcano in the Tôya lake Tôya caldera depression Tp _{h2} (13900 ± 250 yrs. B.P.) (GaK-521)* Tp _{h1} (25000 ± yrs. B.P.)*		
		Takinoue welded tuff Sobetsu pumice-flow deposit (partly welded tuff) (?) Basement volcanic rock of 554 m. peak				
Neogene Tertiary		Osaru-gawa formation				
Miocene						

* after MINATO (1966)

ash, massive and scarcely solidified, and contain rhyolitic pumice ($\text{SiO}_2=70.9\%$) and andesitic lithic fragments. Neither joint nor stratification can be observed, except for faint false-bedding at the upper most part of the deposits. The $<2\ \mu$ clay content of the upper horizon of the Tôya pumice-flow deposits is about 5–10% (wt).

Usu c pumice-fall deposit (Uc): A pumice-fall deposit, 2–3 m in thickness, is distributed around the Tôya caldera, covering the Tôya pumice-flow 2 (Fig. 2, Nos. 1, 7 and 15). This deposit is named as “volcanic ash Uc” (NAGANUMA *et al.*, 1933), and considered to have been derived from the Nakajima volcano which erupted at the center of the caldera (KONDÔ, 1962).

The Uc pumice-fall deposit is mainly composed of dacitic pumice ($\text{SiO}_2=67.6\%$) and contains 5–14% (wt) of $<2\ \mu$ clay at the upper most horizon.

Usu somma: Formation of the Usu somma began in the early Holocene with pouring out of a small amount of olivine basalt lava; the eruption then became violent, and alternative eruptions of lavas and scoria of basalt to mafic andesite took place. Thus a stratocone was completed. Finally, a small quantity of lava and scoria of pigeonite andesite flowed down the eastern flank of the cone (ÔBA, 1966).

After a quiescence, the summit was broken by a strong phreatic explosion, causing the Zenkôji mud-flow which descended the southern flank. Thus, the Usu volcano became a truncated strato-cone, crowned with a circular crater, 1.7 km. in diameter. KONDÔ (1962 and 1963) and YAMADA *et al.* (1963) suggested that the completion of the somma was about 2000–2400 yrs. ago, from the archaeological evidences of human remains found beneath the Zenkôji mud-flow deposit.

The somma is constituted of numerous alternations of thin lava flows and scoria beds (up to 5 m in thickness). No unconformable boundary can be found among these successive members. The uppermost horizon of the scoria-fall and -flow deposits on the eastern flank of the somma has been weathered during a long period, probably more than 1500 years, and it contains about 7–8% of $<2\ \mu$ clay. This weathered surface is covered by a younger pumice deposit (Usu b pumice-fall) with a sharp boundary.

Pyroclastic deposits of the final stage of the Usu volcano: As illustrated in Table 2, the activities of the final stage of the Usu volcano took place in various forms of pumice-fall, ash-fall, nuée ardente, and extrusion and intrusion of lava. These activities were essentially caused by a dacite magma, differing from those of the stratocone-building stage.

KONDÔ (1962) suggested that the Ko-Usu lava dome extruded just after the eruption of the Ub pumice-fall, then activities of Ô-Usu lava dome succeeded. Recently, Meiji-Shinzan (alias Yosomiyama) a crypto-lava-dome, was formed in 1910, and Shôwa-Shinzan, a new steep-sided lava dome, extruded during 1943–1945 (ÔMORI, 1911; SATÔ, 1913; MINAKAMI, 1944 and 1947; FUKUTOMI and ISHIKAWA, 1944; ISHIKAWA, 1947 and 1950; MINAKAMI *et al.*, 1951; YAGI, 1949

and 1953; MIMATSU, 1962).

These activities of the final stage are listed chronologically in the following table:

Table 2. Activities of the final stage of the Usu volcano

Ejection of pyroclastic deposits	Extrusion and intrusion of dome lava
Ua ₀ ash fall=1943-1945	Shôwa-Shinzan (new lava dome)
Yosomiyama mud-flow=1910	Meiji-Shinzan (crypto-dome)
Tateiwa nuée ardente=1853	
Bunsei nuée ardente=1822	
Ua ₁ ash fall=1768 (or 1822 ?)	
Ua ₂ ash fall=1663	Ô-Usu (lava dome)
Ua ₃ ash-fall	
Ua ₃ mud-flow about 350-500 yrs. ago	Ko-Usu (lava dome)
Ub pumice-fall	

Although these younger pyroclastic deposits of the Usu volcano were erupted in recent years, most of them contain as much as 16% (wt) of $<2 \mu$ clay. Obviously, such highly weathered materials did not come directly from magma, except for the Ub pumice-fall deposit. It is considered that they were most likely derived from the clastic materials which had been already weathered (KONDÔ, 1962 and 1963).

CHAPTER 3. EXPERIMENTS FOR THE DETERMINATION OF CLAY MINERALS

a) General properties of the samples

The localities of samples and the columnar sections of pyroclastic deposits are shown in Figs. 1 and 2, and general properties of eighteen bulk samples are given in Table 3.

General properties of each bulk sample were investigated by conventional methods, that is, mechanical analysis by pipet method, measurement of pH by glass electrode method, and determination of oxidation-reduction potential (Eh) by platinum electrode method. The pH value of these samples ranges from 6.8 to 8.0 with a few exception. They have higher pH value and higher base saturation than those of common weathered pyroclastic materials in Hokkaido. All the samples have also high value in Eh, so it is safely said that the weathering process has been developed in a chemical environment with oxidizing condition.

The $<2 \mu$ clay content is higher in the younger Usu pyroclastic deposits (Ua₀, Ymfl, and Ua₃) rather than in some of the older deposits (Uc and Tpf₁). The petrological properties of the samples from the younger deposits were examined under the microscope. Actually, microscopic observation showed that primary minerals and lithic fragments included in these samples were indicative of older

Table 3. General properties of the weathered pyroclastic deposits of the Usu volcanic district.

No.	Name of deposit	Petrological properties of deposit	Depth (m)	pH in water	Eh (mV)	Clay (<2 μ) (wt. %)	Main clay minerals*	SiO ₂ /Al ₂ O ₃ (mol.) of clay fraction
61 U 122	Shōwa-Shinzan ash-fall	andesite	0.2	5.9	468	13.7	K-M	6.1
60 U 94	Yosomiya mud-flow	andesite	0.8	7.9	379	16.3	K-M	4.7
60 U 12	Usu a ₃ ash-flow	mafic andesite	2.3	7.6	416	n.d.	K-M	5.0
60 U 10	Usu a ₃ ash-flow	mafic andesite	2.6	7.7	391	n.d.	K-M	5.2
61 U 131	Usu a ₃ ash-flow	mafic andesite	0.4	7.5	409	7.0	K-I-M/C-M	n.d.
61 U 132	Usu a ₃ ash-flow	mafic andesite	0.6	7.1	411	4.8	K-I-M/C-M	5.1
60 U a ₃	Usu a ₃ ash-fall	mafic andesite	0.5	7.3	427	n.d.	K-M/C-M	5.8
60 U 55	Somma scoria-fall	mafic andesite	5.1	7.8	378	5.7	B-Allo	2.9
60 U 24	Somma scoria-fall	mafic andesite	10.3	8.0	376	2.4	K-M	4.6
60 U 17	Usu c pumice-fall	dacite	13.1	7.8	382	5.2	K-C-I	4.6
60 U 101	Usu c pumice-fall	dacite	1.2	7.2	419	n.d.	K-M	n.d.
60 U 99	Usu c pumice-fall	dacite	1.4	7.3	411	14.0	K-I-C-M	5.2
61 U 134	Usu c pumice-fall	dacite	3.5	7.6	396	2.8	I-H/H.H.	3.8
61 U 135	Toya pumice-flow 2	rhyolite	2.8	7.3	414	10.6	C-I-H/H.H.	n.d.
61 U 133	Toya pumice-flow 2	rhyolite	5.8	7.7	392	5.7	I-C-H/H.H.	4.2
60 U 47	Toya pumice-flow 2	rhyolite	8.2	7.0	433	10.3	K-M/Vt	4.4
61 U 130	Toya pumice-flow 1	rhyolite	7.4	6.8	456	2.0	K-M/14 Å-M	5.0
61 U 129	Toya pumice-flow 1	rhyolite	7.7	6.8	441	5.4	K-I-14 Å	n.d.

* M: Montmorillonite, H: Halloysite, H.H.: Hydrated halloysite, I: Illite, Vt: Vermiculite, C: Chlorite, K: Kaolin minerals, M/C: Mixed-layer mineral of montmorillonite-chlorite, Allo: Allophane, 14 Å: 14 Å minerals, B: Boehmite, H/H.H.: Random mixed-layer mineral of hydrated halloysite and halloysite, M/Vt: Mixed-layer mineral of montmorillonite-vermiculite, M/14 Å: Mixed-layer mineral of montmorillonite-14 Å mineral

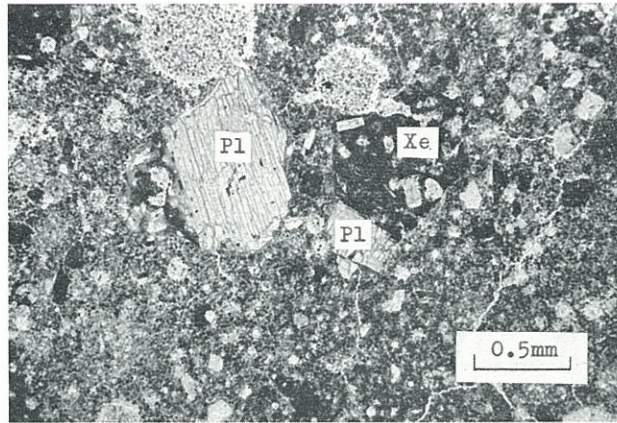


Fig. 3. Partially weathered lava fragment found in the Usu a₃ ash.

Xe: fragment of the Usu somma lava

Pl: plagioclase

mafic andesite origin. For example, a sample from the Ua₃ deposit is mainly composed of fine fragments of altered mafic andesite (Fig. 3).

The weathered pyroclastic deposits in this district are found to have some peculiar characteristics. Differing from other felsic pyroclastic deposits in Hokkaido, these deposits contain a considerable amount of montmorillonite, mixed-layer mineral of montmorillonite and chlorite, and other 2:1 type clay minerals in clay fraction. However, no halloysite can be found in the Usu pyroclastic deposits, although it is included in the Toya pumice-flow deposits in the deeper horizon from the surface.

For the present study, the $<2\ \mu$ clay samples from these deposits were separated and investigated by the following treatments.

b) X-ray diffraction analysis

Minerals falling into the $<2\ \mu$ fraction were identified by means of X-ray diffraction. X-ray diffraction patterns were obtained by the "Philips Geiger Counter X-ray Spectrometer" with filtered Cu K α radiation. The experimental conditions were 35 Kv., 13 mA., time constant 4 seconds, scanning speed 2° per min., angular aperture 1°, and receiving slit 0.006 inch.

The oriented samples were prepared from clay pastes which were spread on silica slide-glass, the latter having been proved suitable for heating tests. X-ray diffraction patterns of the $<2\ \mu$ clays are shown in Figs. 4, 5, and 6. To ascertain the nature of the basal reflections of clay minerals, the effects of treatment with several reagents and heating tests on X-ray diffraction patterns were investigated. The procedure was modified from the method of OINUMA *et al.* (1961). The results are shown in Figs. 7-15. Summarizing the analysis of these patterns, the following results were obtained.

It is clear that a sample from the Shōwa-Shinzan ash-fall deposit (Ua_0) is mainly composed of montmorillonite with basal reflection of 15.8 Å (001). Further checks were made by heating at 300°–1000°C for one hour, and treatment with ethylene glycol (WALKER, 1958). The 15.8 Å spacing contracted to near 10 Å after heating at 400°C, while it expanded to 17 Å after ethylene glycol solvation (Fig. 7, 61 U 122). The spacing of (06) or (060) is 1.512 Å, which is assigned to that of the dioctahedral montmorillonite. The 7.0 Å reflection may correspond to a presence of small amount of kaolin minerals, while 4.09 Å that of α -crystalite. A sample of the Yosomi-yama mud-flow deposit is also mainly composed of montmorillonite (Fig. 4, 60 U 94).

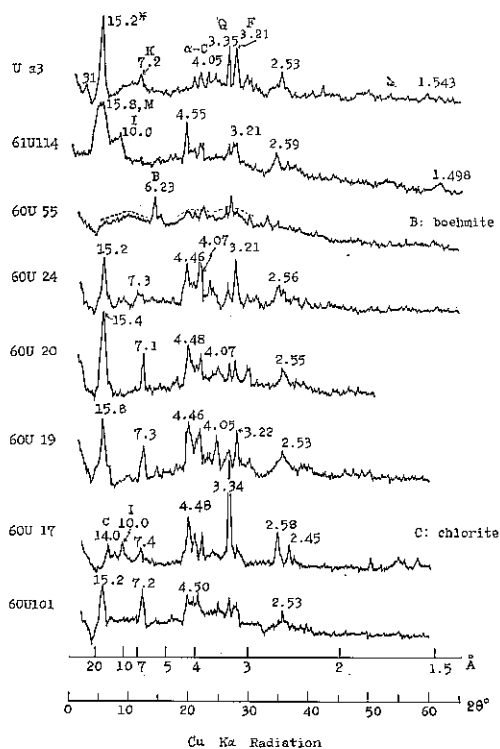


Fig. 5. X-ray diffraction patterns of clays (2).

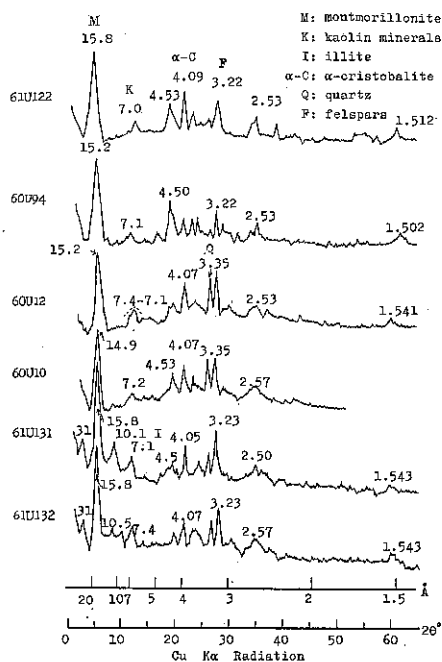


Fig. 4. X-ray diffraction patterns of clays (1).

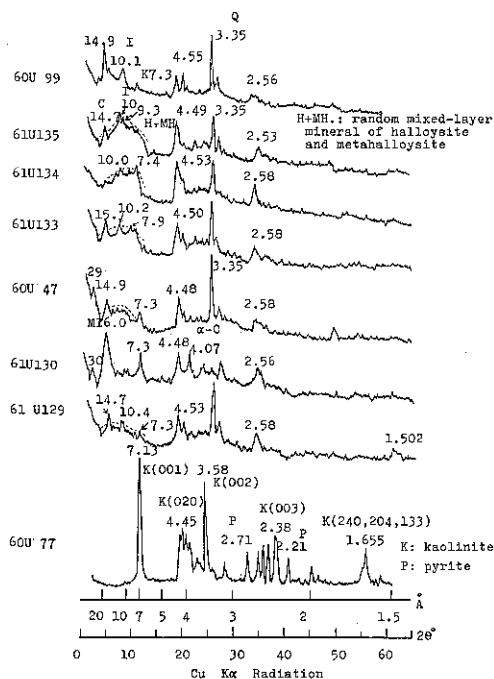


Fig. 6. X-ray diffraction patterns of clays (3).

Samples of the Ua_3 ash-fall and mud-flow deposits are rich in expanding 2:1 type clay minerals which are referred to iron-rich montmorillonite and regular mixed-layer mineral of montmorillonite-chlorite. The 15 Å reflection of these samples are scarcely affected by saturation with ethylene glycol and/or water (Figs. 4 and 5, 60 U 10 and Ua_3). SAWHNEY (1960) indicated that interlayer materials, especially Al-hydroxyls, prevented montmorillonite from expanding to 17–18 Å for the ethylene glycol and Mg-glycerol tests. The 15 Å spacing, however, are expanded to near 17 Å spacing after TAMURA's treatment (1 N Na-citrate for 8 hours before ethylene glycol solvation) (TAMURA, 1958). Due to a treatment with 1:10 HCl for 30 minutes, the 15 Å reflection completely disappeared (Figs. 8 and 9, 60 U 12 and 61 U 132). From the tests above mentioned, it is suggested that the characteristic feature of the montmorillonite in these samples would be attributable to Al in the interlayer space and a small amount of interstratified chlorite (Ferich) layer.

A clay mineral with long spacing of about 30 Å was found in some of the samples from the Ua_3 ash-fall deposit (Figs. 4, 5, and 9, 61 U 131, Ua_3 , and 61 U 132). The 31 Å reflection was shifted to 32 Å, and the 15.8 Å reflection to 17 Å after a treatment with ethylene glycol. The 31 Å reflection was persistent at a temperature range from 20° to 150°C, but completely collapsed above 300°C. The 15.8 Å reflection contracted to 14.7 Å at 300°C, which was persistent up to 400°C, but disappeared above 600°C. Owing to a treatment with 1:10 HCl, the 31 Å

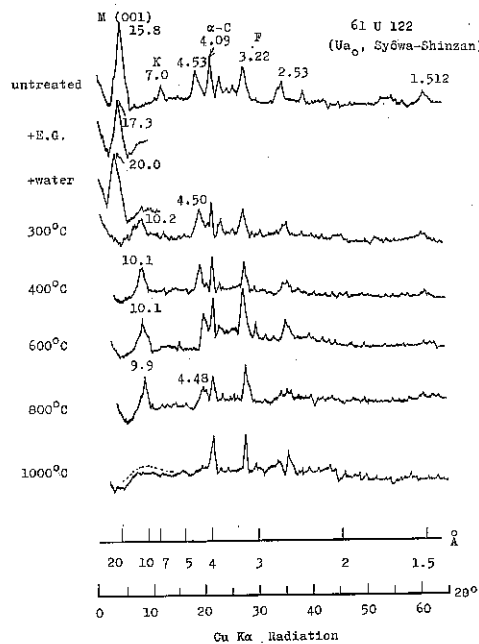


Fig. 7. X-ray diffraction patterns of clay after various treatments (1).

+E.G.: treated with ethylene glycol.

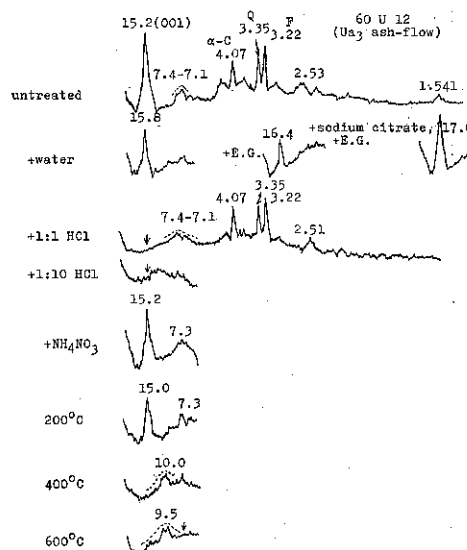


Fig. 8. X-ray diffraction patterns of clay after various treatments (2).

+Sodium citrate, +E.G.: treated with ethylene glycol and 1 N sodium citrate.

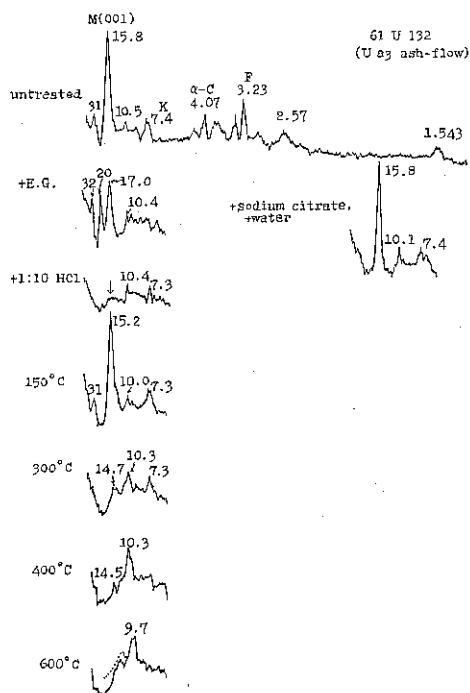


Fig. 9. X-ray diffraction patterns of clay after various treatments (3).

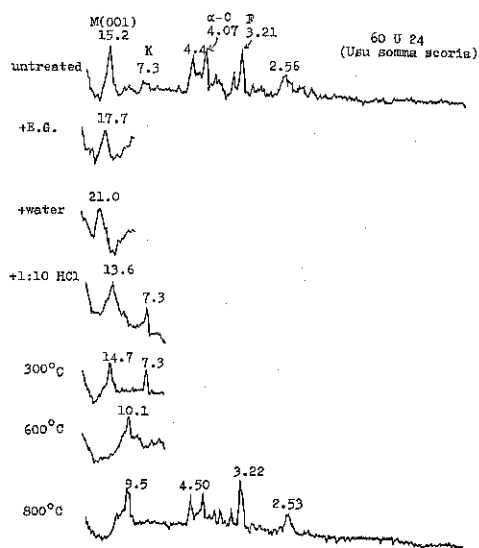


Fig. 10. X-ray diffraction patterns of clay after various treatments (4).

and 15.8 Å reflections completely disappeared (Fig. 9). From the above tests, the unusually long spacing of about 30 Å is considered to be formed as the result of a regularly alternating stacking of montmorillonite and chlorite lattices. Montmorillonite, illite, and kaolin minerals were also detected in these samples by means of X-ray analysis.

X-ray diffraction pattern of the clay fraction of the humic soil from the scoria-fall deposit showed only a weak reflection at 6.32 Å. This sample consists of amorphous allophane-like material and a small amount of boehmite (Fig. 5, 60 U 55). On the other hand, the weathered scoria-fall deposit in the deeper horizon from the surface, is mainly composed of montmorillonite (Fig. 10, 60 U 24). Both facts suggest that the weathering of mafic scoria deposit takes place in two different modes; one is the formation of colloids of kaolinite-type under the optimum leaching, and the other is that of the clay mineral of montmorillonite-type under the alkaline environment at the deeper horizon where the active leaching is actually interrupted.

X-ray diffraction patterns of the samples from the Usu c pumice-fall deposit, however, do not show the same tendency. From the clay mineral composition, these samples can be divided into two groups. The first one is characterized by richness in the 2:1 type clay minerals such as montmorillonite, chlorite, and illite. Some 7 Å kaolin minerals are also detected in this group (Figs. 5 and 11, 60 U 17, 60 U 101, and 60 U 99). On the other hand, the second group is mainly composed of the mixed-layer mineral of hydrated halloysite with a small amount of

14 Å minerals, illite, and mixed-layer mineral of illite and 14 Å mineral (Fig. 12, 61 U 134).

Mixed-layer mineral of hydrated halloysite and halloysite, illite, and "clay chlorite" are found in some samples of the Tōya pumice-flow deposit 2 (Tpfl₂) (Figs. 6 and 13, 61 U 135 and 61 U 133). "Clay chlorite" can be identified with respect to its disintegration temperature which is lower than that of the normal chlorite (BROWN, 1961, p. 263-264). One of the samples of this pumice-flow deposit, is mainly composed of a regular mixed-layer mineral of montmorillonite-vermiculite (Fig. 14, 60U47).

Samples from the Tōya pumice-flow deposit 1 (Tpfl₁) are dominant in some

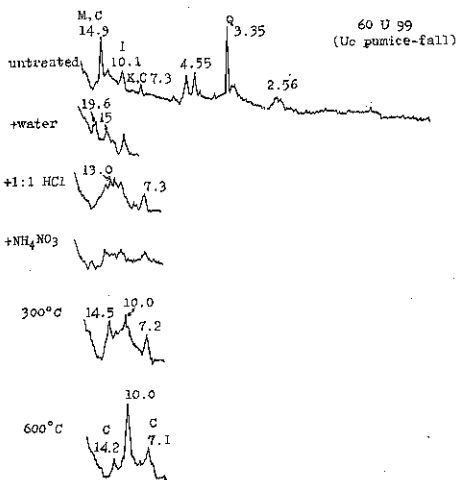


Fig. 11. X-ray diffraction patterns of clay after various treatments (5).

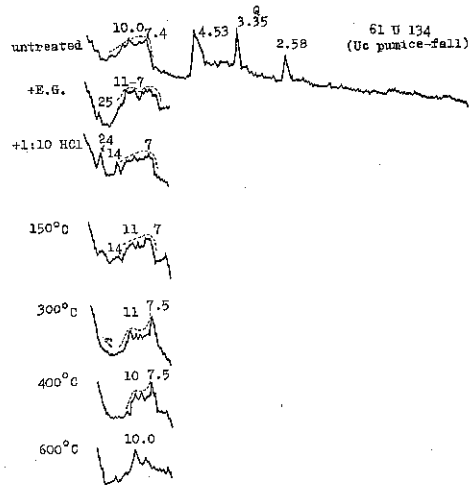


Fig. 12. X-ray diffraction patterns of clay after various treatments (6).

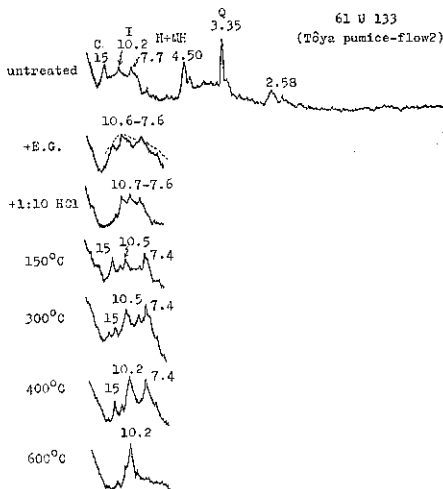


Fig. 13. X-ray diffraction patterns of clay after various treatments (7).

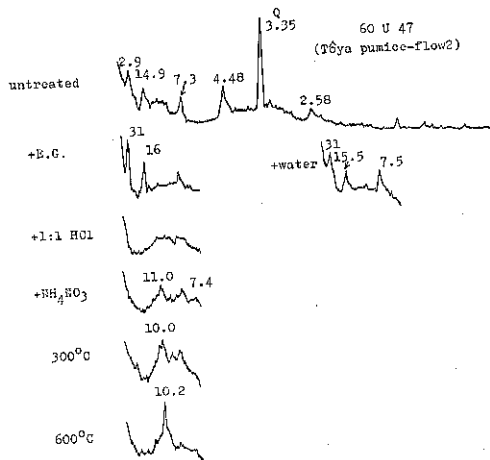


Fig. 14. X-ray diffraction patterns of clay after various treatments (8).

expanding 2:1 type clay minerals, namely montmorillonite, and a regular mixed-layer mineral of montmorillonite-14 Å mineral. A small amount of 7 Å kaolin minerals is also found (Fig. 15, 61 U 130). Another sample is abundant in 14 Å minerals, illite and 7 Å kaolin minerals (Fig. 6, 61 U 129). Such difference in clay mineral composition will be discussed later.

c) Infra-red spectra

Measurements were made by the Kôken Infra-red Spectrophotometer model DS-301 using a NaCl prism. Air-dried 3.0 mg clay sample was well mixed with powdered 300 mg KBr, and pressed into transparent disc under vacuum (100kg/cm²). The infra-red spectra in the NaCl region, 2.5-16 μ , are shown in Fig. 16.

Assignments of the infra-red spectrum bands of these samples were determined using the available data on synthetic clay minerals (STUBIČAN and ROY, 1961 a and b). The montmorillonite-rich samples are characterized by the absence of a sharp band at 11.2 μ (Fig. 16, 60 U 10, 61 U 132, 60 U a₃, and 60 U 24). The infra-red spectra of these samples almost agree with those of nontronite or iron-rich variety of montmorillonite group (WIEDEN, 1960). Pure specimen of nontronite, however, displays a prominent spectrum band at 12 μ due to the O-H-Fe³⁺ vibration in the octahedral layer (STUBIČAN and ROY, 1961b; SERRATOSA, 1962). Accordingly, it seems reasonable to assume that these samples are mainly composed of iron-rich varieties of montmorillonite.

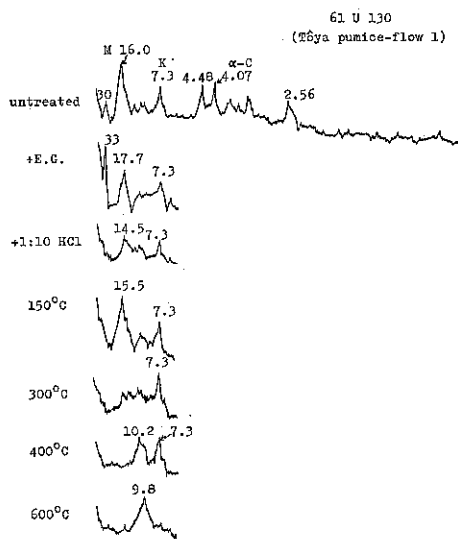


Fig. 15. X-ray diffraction patterns of clay after various treatments (9).

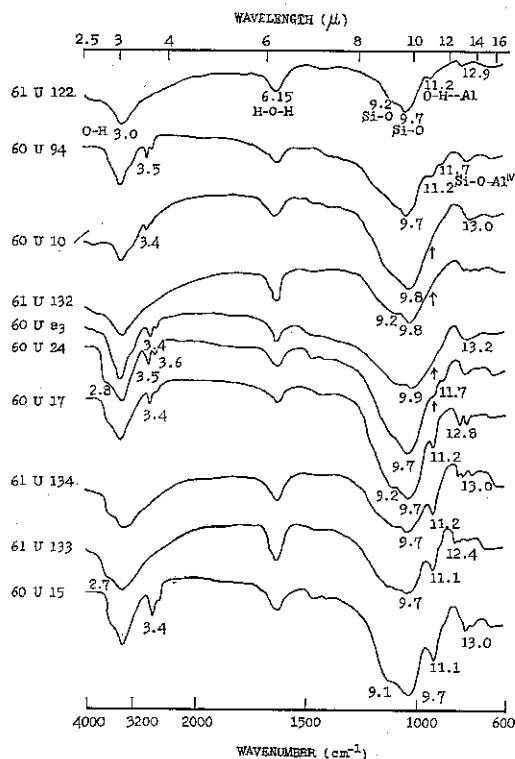


Fig. 16. Infra-red spectra of clays.

The halloysite mineral-rich samples display the major-absorption bands in the infra-red spectra at 9.2 and 9.7μ (two bands), and a sharp band at 11.2μ caused by the O-H--Al³⁺ vibration in the octahedral layer.

d) Differential thermal analysis

Heating rate for differential thermal analysis was 10°C per minute. The differential thermal curves of four typical samples are shown in Fig. 17.

The differential thermal curve of the sample 61 U 122 exhibits five endothermic peaks at 135° , 230° , 565° , 760° , and 855°C . The clear doublet peaks at 135° and 230°C are due to hygroscopic moisture and adsorbed water on exchange cations in clays. These peaks prove that the sample 61 U 122 is mainly composed of montmorillonite, as expected from the result of X-ray analysis.

The sample 60 U 12 shows six endothermic peaks at 145° , 230° , 595° , 705° , 750° and 805°C , and a weak exothermic peak at 930°C . The endothermic peaks in a range of 600° – 800°C are caused by dehydration of structural OH of the 2:1 type clay minerals. These peaks may be attributed to both montmorillonite and other clay minerals of 2:1 type which were identified by X-ray diffraction and IR spectra as mentioned before.

On the other hand, the curve of the sample 61 U 134 exhibits a sharp endothermic peak at 560°C , and a clear exothermic peak at 940°C . Both peaks are assigned to the fact that the sample is abundant in low-crystalline halloysite minerals as stated before. The sample 61 U 133 shows five endothermic peaks at 140° , 230° , 550° , 700° – 770° and 815°C , and a clear exothermic peak at 910°C .

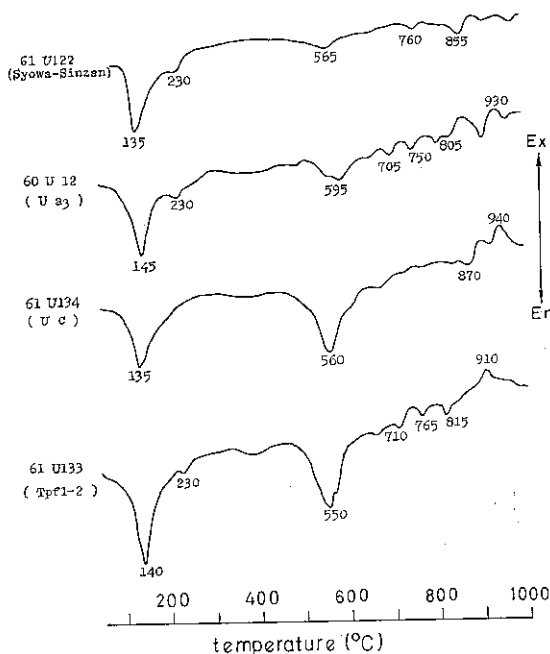


Fig. 17. Differential thermal analysis curves of clays.

This curve is consistent with the result of X-ray diffraction and IR spectra which shows that the sample includes both 2:1 type clay minerals and low-crystalline halloysite minerals.

e) Chemical analysis

Chemical analysis was carried out for the fourteen clay samples, as shown in Table 4. Eight samples (61 U 122-60 U 24) from the younger Usu pyroclastic deposits are rich in SiO_2 , CaO , Fe_2O_3 and alkalis, and poor in Al_2O_3 , with only one exception. Their $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (mol) ranges from 4.6 to 6.0, being equivalent to montmorillonitic clay.

As for six samples (60 U 17-61 U 130) from the older pyroclastic deposits, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio decreases in a range from 3.8 to 5.2. Moreover, these samples are poor in CaO , MgO , and Na_2O . Relative enrichment of K_2O is found in the samples of 60 U 17 and 60 U 99, owing to a presence of illite as expected from the X-ray diffraction analysis (Figs. 5 and 11).

$\text{SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}^\pm$ relation of the analysed clay samples from this district, is shown in Fig. 18. The same relation of the clay fractions derived from felsic pyroclastic deposits in Japan (OSSAKA, 1960; KANNO *et al.*, 1956 b and 1961 a; ISHII and KONDÔ, 1962 a and b) and that of glassy volcanic ejecta in Hokkaido (KATSUI, 1962), are also plotted in the diagram for comparison. It is clearly shown that the clay samples of the Usu district are rich in SiO_2 and poor in Al_2O_3 and H_2O^\pm , being equivalent to the composition of montmorillonitic clay.

Table 4. Chemical compositions of clays. (Per cent on air-dried basis).

	61U 122	60U 94	60U 12	60U 10	61U 132	60U a ₃	60U 55	60U 24	60U 17	60U 99	60U 134	61U 133	60U 47	61U 130
SiO_2	51.23	43.96	43.17	47.32	42.94	50.51	31.32	47.35	49.14	52.32	41.96	45.09	45.62	46.73
Al_2O_3	14.30	15.98	14.55	15.35	14.37	14.65	18.30	17.57	17.98	17.20	18.90	18.32	17.75	15.95
Fe_2O_3	7.41	12.08	11.70	12.19	8.00	6.45	6.74	13.77	10.10	8.91	9.73	8.64	10.20	8.89
FeO	1.19	0.83	2.21	1.88	2.23	3.62	4.23	0.55	0.75	0.41	0.35	0.32	0.38	0.49
CaO	3.17	4.18	3.50	4.03	3.17	3.27	4.62	2.32	0.85	1.35	0.45	0.80	0.70	1.65
MgO	1.84	0.34	2.96	2.05	1.59	2.59	0.42	1.29	0.12	0.34	0.19	0.90	0.10	0.27
Na_2O	1.16	1.01	2.59	2.59	2.55	4.10	0.51	1.17	0.79	0.84	0.43	0.66	0.86	0.85
K_2O	0.79	0.72	1.29	1.01	1.21	1.20	0.71	0.49	1.83	1.80	1.02	1.42	1.69	0.41
$\text{H}_2\text{O} (-)$	9.61	10.69	9.60	4.93	13.17	8.98	10.57	8.24	9.90	8.49	12.62	11.41	12.95	12.77
$\text{H}_2\text{O} (+)$	8.76	9.65	7.86	8.24	10.14	4.39	22.13	7.02	8.13	8.53	14.37	12.07	9.49	11.39
Total	99.46	99.44	99.43	99.59	99.37	99.76	99.55	99.77	99.59	100.19	100.02	99.63	99.74	99.40
$\text{SiO}_2/\text{Al}_2\text{O}_3$	6.1	4.7	5.0	5.2	5.1	5.8	2.9	4.6	4.6	5.2	3.8	4.2	4.4	5.0

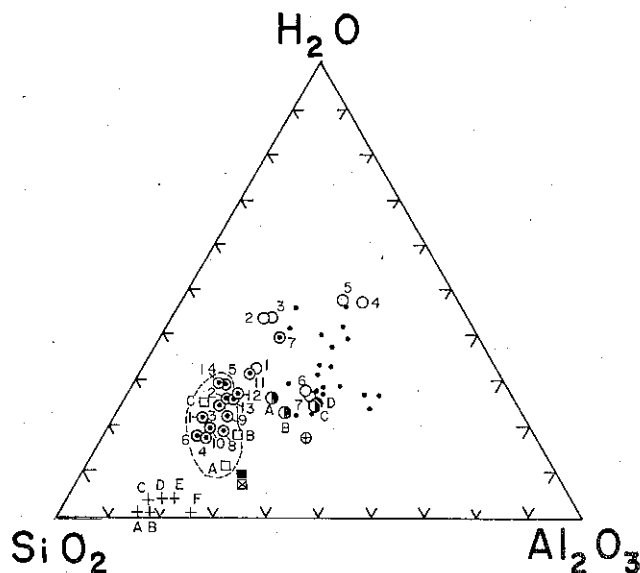


Fig. 18. $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ diagram of clays and clay minerals.

- 1-7: Pumiceous clays in the Sapporo-Tomakomai lowland district.
 ⊙ 1-4: Clays in the Usu volcanic district. +A: Volcanic glass of the pumice erupted from the Komaga-take. +B: Obsidian glass (average of 3). +C: Rhyolitic pumice. +D: Dacitic pumice (average of 5). +E: Andesitic pumice (average of 2). +F: Mafic andesitic scoria (average of 2). ●: Allophanic clays. (Ossaka, 1960)
 ⊕ A-D: Hydrated halloysite. ⊕ Halloysite (average of 14).
 □ A-C: Montmorillonite. ⊠ Clay of the Shinmoidake ash (beidelite like montmorillonite) (after Kanno et al., 1959, 1961 a) ■ Illite.

f) Electron micrographs

Electron micrographs of the clay samples were taken by the electron microscope of Hitachi Laboratory's model HS-6. For the preparation of samples, the $<2\ \mu$ clays were dispersed on collodion membrane by the technique of water-paste method, then they were shadowed by chromium and strengthened by carbon evaporation.

The sample from the Shōwa-Shinzan ash-fall deposit (Ua_0) consists of irregular, but more or less equidimensional, flakes which are so thin that their edges are difficult to be discerned against the background. In consequence the aggregates show a "fluffy" appearance, typical of most of montmorillonites. Some montmorillonite particles, however, are characteristically lath-like shaped (Plate I, Fig. 1). Some particles of the montmorillonite from the mud-flow deposit (Ua_3), are also lath-like shaped flocking into elongated bundles (Plate II, Fig. 1). Although no definite identification is given for these particles, some estimations are allowed with reference to the results obtained from the other analyses already mentioned. At least some of the lath-shaped particles may be nontronitelike montmorillonite (MARSHALL *et al.*, 1942; BATES, 1958).

Another flocks of very fine particles (0.02μ) are observed in the electron micrographs of clay fraction of humic soil derived from the scoria-fall deposit. Judging from the data of chemical analysis and X-ray diffraction pattern, these flocks may be allophanic materials. On the other hand, the sample from the weathered scoria-fall deposit in the deeper horizon from the surface, consists of "fluffy" aggregates peculiar to montmorillonite (Plate III, Fig. 1), accompanied with lath-shaped and ribbon-like particles. These peculiar particles may be nontronite-like or iron-rich montmorillonite, as referred before.

Electron microscopic figures of the samples from the Usu c pumice-fall deposit, reveal to consist of thin tabular, lath, tubular and the other shapes of clay particle (Plate IV, Fig. 1 and 2). Some of the thin tabular particles and lath-shaped ones may be illite. The tubular particles are considered to be halloysite as detected by the X-ray diffraction analysis.

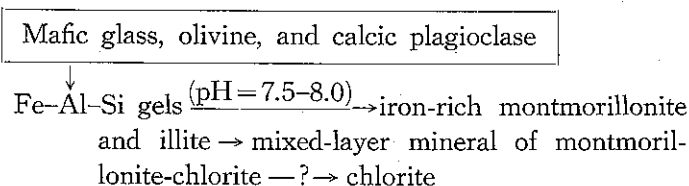
CHAPTER 4. WEATHERING PROCESS

Mode of the weathering process of the pyroclastic deposits in this district, is found to have some peculiar characteristics compared with that of the felsic pyroclastic deposits in the other regions of Hokkaido. These weathered deposits contain a considerable amount of montmorillonite, mixed-layer mineral of montmorillonite and chlorite, and the other 2:1 type clay minerals. However, halloysite which is the most common clay mineral in the felsic pyroclastic deposits in Hokkaido, is scarcely found in the younger Usu pyroclastic deposits. Therefore, it must be considered that the process leading to the formation of montmorillonite contrasts with that of kaolin minerals.

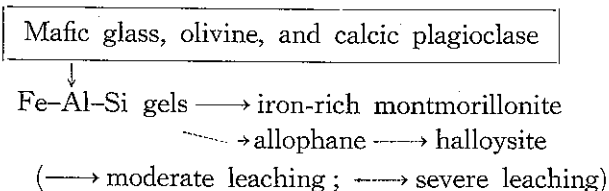
From the field observation and microscopic examination, it is pointed out that the younger pyroclastic deposits of Ua₆, Yosomiyama mud-flow, Ua₃ ash-fall, and mud-flow are of secondary origin, as mentioned already. The characteristic clay minerals included in them are of the 2:1 type. On the basis of these data, it seems to be reasonable that these 2:1 type clay minerals were not formed by the normal surface weathering, but produced from the mafic pyroclastics under alkaline and wet condition which prevailed at the deeper horizon from the surface. In such environment, mafic glass and olivine are apt to alter into iron-rich montmorillonite, illite, and mixed-layer mineral of montmorillonite-chlorite. It is noticed that the pyroclastic materials including such clay minerals were intermittently ejected during last 500 years of the final stage of the Usu volcano.

The factors for the formation of montmorillonite minerals have been considered as follows: a) chemical character of parent material, b) efficiency of drainage, c) pH value of water, d) climate condition of the weathering environment and others (ROSS and HENDRICKS, 1945; SHERMAN and UEHARA, 1956; KELLER, 1957, p. 65; GRIM, 1958; RICH and KUNZE, 1964, p. 22; SWINDALE, 1966). It is expected that the chemical system in which montmorillonite is formed, will be characterized by a high Si/Al ratio and a relative abundance of Mg, Fe, Ca, Na,

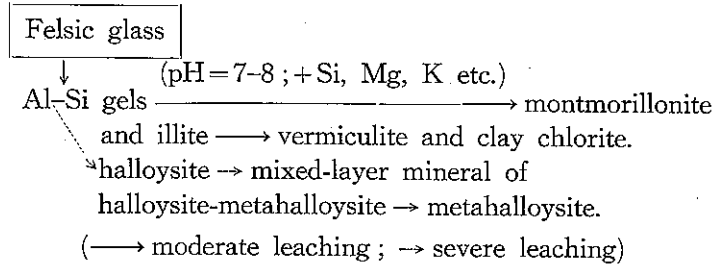
and K, with correspondingly lower concentration of H ions. In terms of parent material, the rocks and pyroclastic deposits of the Usu somma are generally mafic and rich in MgO, FeO, and CaO, enough to supply the cations between the O-Si-Al sheets of montmorillonite clay minerals. Therefore, these parent materials are more likely to alter to montmorillonite than to kaolin minerals. Furthermore, the divalent cations tend to coagulate silica, and convert it into a material concentrated in a water-glass solution. Thus, the high Si/Al ratio of montmorillonite is resulted as discussed by RICH and KUNZE (1964, p. 22). The weathering process of mafic pyroclastics at the deeper horizon in the Usu district is considered to be as follows:



As mentioned before, two different processes of weathering are found in the Usu scoria-fall deposit, i.e. one is the formation of kaolinitic type clay, namely the humic soil composed of allophanic clay and a small amount of boehmite; the other is that of iron-rich montmorillonite. Field and laboratory studies suggest that the formation of kaolinitic type clay was taken place under the severe leaching at the surface condition, while that of the montmorillonitic type clay under alkaline (pH=7.5-8.0) and wet condition at the deeper level as discussed above. The different weathering processes of the scoria-fall deposit, may be considered as follows:

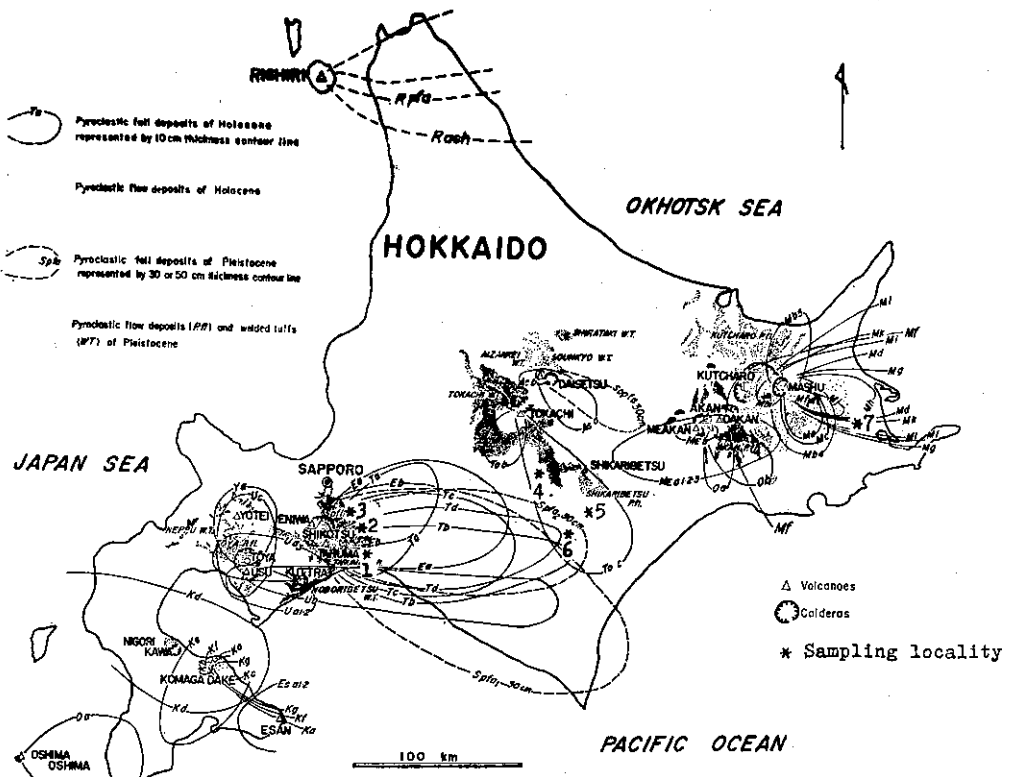


Clay mineral compositions of the Usu c pumice-fall deposit and the Tôya pumice-flow deposits which are overlaid by the younger Usu pyroclastics, are widely fluctuated in different areas, possibly due to the difference in moisture regime and secondary addition of chemical components. Differing from the other felsic pyroclastic deposits in Hokkaido, these burried pumice deposits are composed of low-crystalline kaolin minerals together with montmorillonite, illite, and 14 Å minerals (clay chlorite and vermiculite). Though the paragenesis of clay minerals in each area can not be well explained, some of the 2:1 type clay minerals in these deposits seem to have formed under the high pH condition (7 to 8) with simultaneous addition of silica, magnesium and alkalis from the overlying deposits. Weathering of the felsic pyroclastic deposits in this district is considered to have been taken place by the following processes:



CHAPTER 5. DISCUSSION

Main components of the clay fraction from the most of the pyroclastic deposits of Hokkaido are allophane or low-crystalline halloysite. Most of the felsic pyroclastic deposits in Hokkaido are composed of the non-welded pumices and ashes (Figs. 19 and 20). Their total porosity is usually high and fairly uniform throughout the deposit. Therefore, the permeability coefficient of these deposits is usually greater than 10^{-2} - 10^{-3} cm/sec. Under the excessive moisture and dominant leach-



DISTRIBUTION OF THE QUATERNARY PYROCLASTIC DEPOSITS IN HOKKAIDO
 Fig. 19. Distribution of the Quaternary pyroclastic deposits in Hokkaido. (after YAMADA *et al.*, 1963).

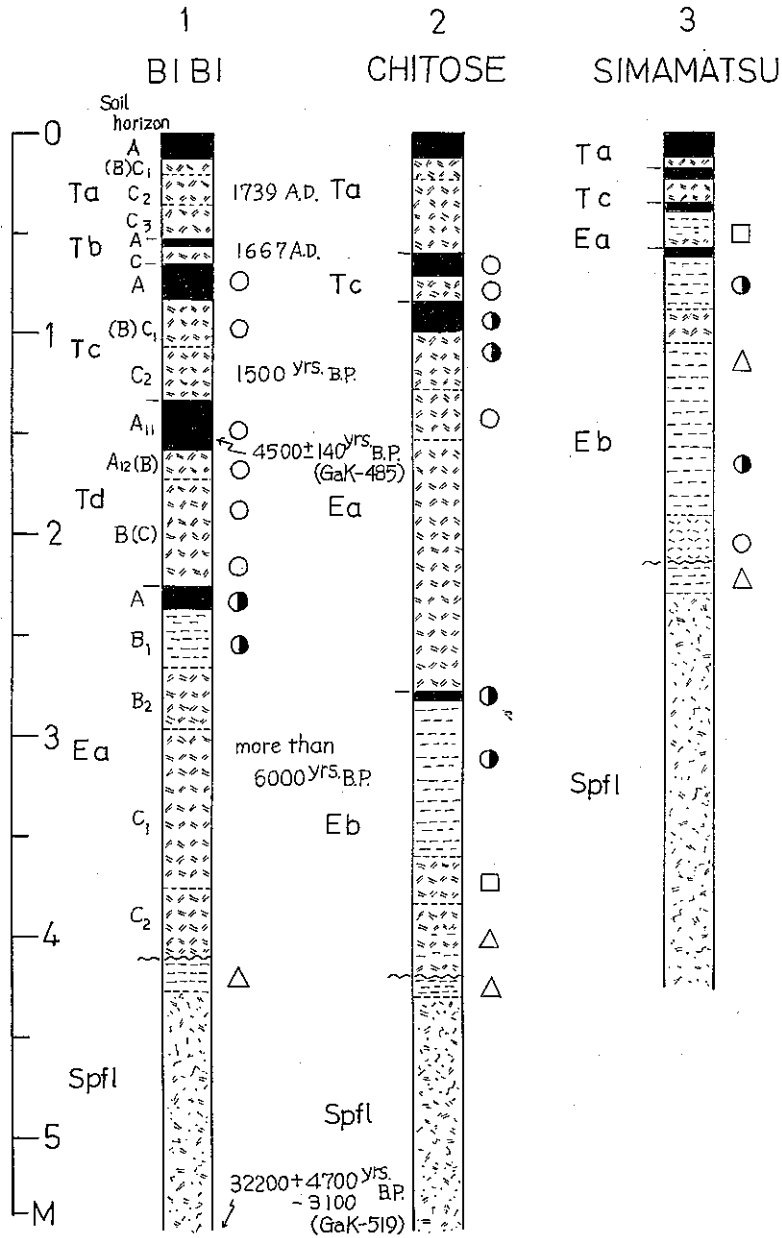
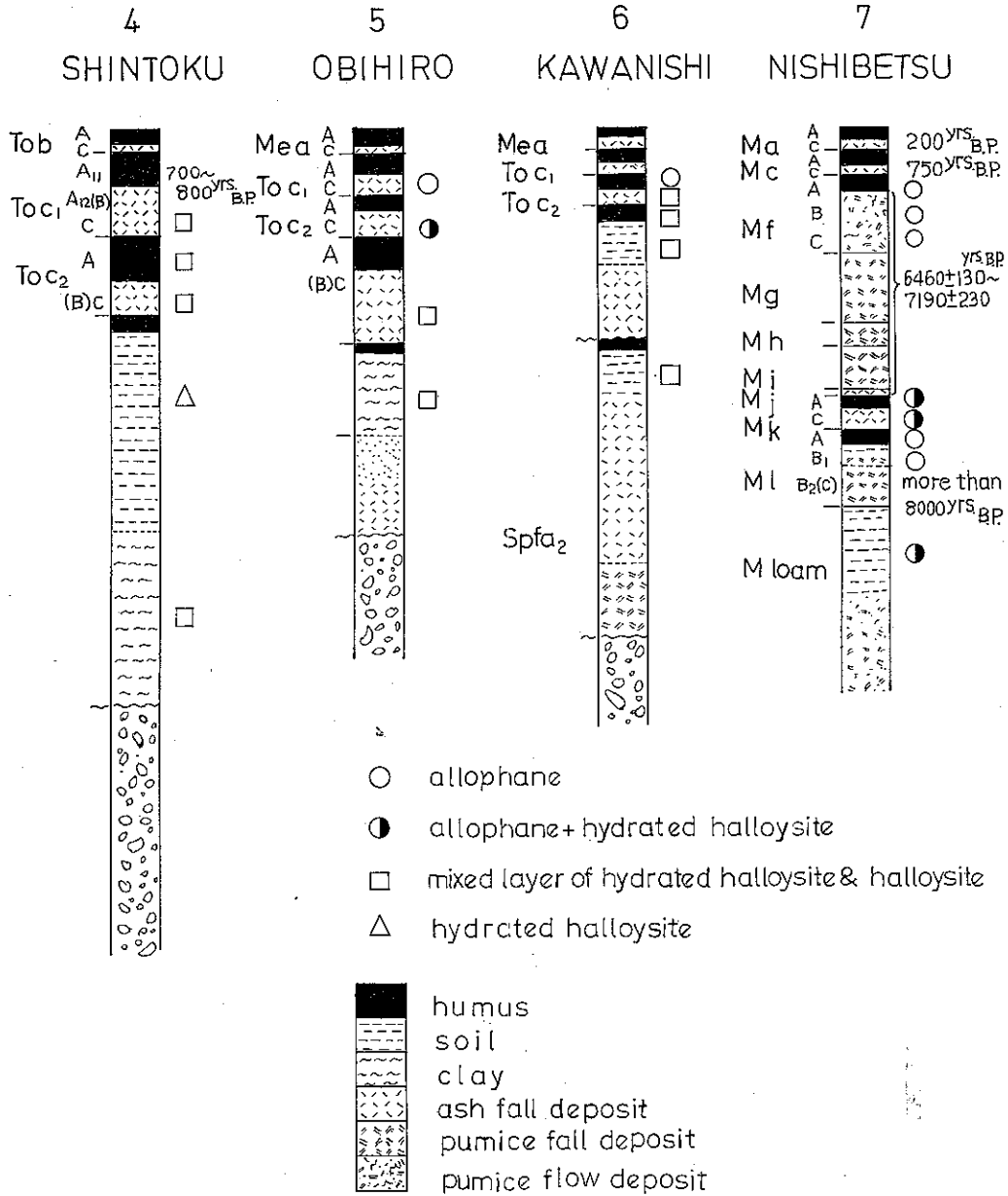


Fig. 20. Columnar sections of the pyroclastic deposits in the southern Hokkaido. (after Ishii and Kondō, 1962 a, b).

ing conditions, where free drainage prevails but it is not droughty throughout the year, the felsic pyroclastic materials undergo desilication together with a remarkable loss of bases. Aluminum and iron remain essentially static during the weathering. A clay fraction consisting of amorphous, highly hydrated silica and alumina, is discrete at first, then forms cross-linking in the early stage of weathering. Due



Number of each column is plotted in Fig. 19.

to strong buffering of alumina, however, this amorphous state may persist for a quite long time. The discrete type of mixed silica and alumina has been called as "allophane B" and the crosslinked type as "allophane A" (FIELDER, 1955 b). The chemical transition from the allophane A to halloysite can be regarded as a continuous process of dehydroxylation through condensation and replacement

Table 5. General properties of the weathered pyroclastic deposits at Hayakita.
(after ISHII and KONDŌ, 1962 a, b).

Deposit	Petrological properties of deposit	Soil horizon	Depth (m)	pH in water	Clay (<2 μ) (wt. %)	Mainly clay minerals	SiO ₂ /Al ₂ O ₃ of clay fraction
Tarumai a pumice-fall	augite-hypersthene andesite	A	0.05	5.3	4.5	Si, Al gels	3.9
Tarumai b pumice-fall	augite-hypersthene andesite	C	0.12	5.7	0.1	Si, Al gels	—
Tarumai c pumice-fall	augite-hypersthene andesite	A	0.18	5.8	0.4	Si, Al gels	3.4
Tarumai d pumice-fall	augite-hypersthene andesite	A ₁₁	0.45	5.5	7.1	allophane	—
Eniwa a pumice-fall	augite-hornblende dacite	A ₁₂ (B)	0.55	5.8	1.3	allophane	0.9
Eniwa b pumice-fall	augite-hornblende dacite	C	0.65	6.3	0.5	allophane	—
Shikotsu 1 pumice-fall	augite-hornblende dacite	A ₁₁	0.85	5.8	4.3	allophane	—
Shikotsu 2 pumice-fall	augite-hornblende dacite	A ₁₂	1.00	6.0	1.2	allophane	—
Shikotsu 3 pumice-fall	augite-hornblende dacite	B	1.25	6.5	0.5	Fe gels-allophane	1.3
Shikotsu 4 pumice-fall	augite-hornblende dacite	A	1.93	5.8	4.8	allophane-hydrated halloysite	—
Shikotsu 5 pumice-fall	augite-hornblende dacite	B (C)	2.20	5.8	3.3	allophane-hydrated halloysite	2.1
Shikotsu 6 pumice-fall	augite-hornblende dacite	A (B)	2.55	6.0	1.4	allophane-hydrated halloysite	—
Shikotsu 7 pumice-fall	augite-hornblende dacite	1	3.15	6.2	7.0	hydrated halloysite	1.9
Shikotsu 8 pumice-fall	augite-hornblende dacite	3	6.90	5.8	8.0	hydrated halloysite	—
Shikotsu 9 pumice-fall	augite-hornblende dacite	1	6.95	6.2	9.7	hydrated halloysite	—
Shikotsu 10 pumice-fall	augite-hornblende dacite	3	8.70	5.0	6.8	14 Å minerals-hydrated halloysite	—
Shikotsu 11 pumice-fall	augite-hornblende dacite	—	9.55	5.0	15.6	hydrated halloysite	—
Shikotsu 12 pumice-fall	augite-hornblende dacite	—	14.60	6.0	24.8	hydrated halloysite	—

with silica tetrahedra.

According to ISHII and KONDO (1962 a, b), some felsic pyroclastic deposits in Hokkaido, corresponding to the early stage of weathering, retain clay fractions of the similar allophanic composition. The residual silica and alumina tend to be reoriented producing layer-silicates; first halloysite, secondly mixed-layer mineral of halloysite-metahalloysite, and lastly metahalloysite (Fig. 20, Table 5). According to them, the 61 samples studied by them are mostly of dacitic and rhyolitic, and the environments of sedimentation are well drained and aerated. So, the weathering of these deposits seems to have taken place under the acidic ($\text{pH}=5.3-6.5$) conditions near the surface. In this connection, the depth of the weathered deposits is generally within 5 meters from the surface, and never exceeds 15 meters. It is worthy to note here that allophane is found in the pyroclastic deposits younger than 5000 yrs., while halloysite and/or mixed-layer mineral of halloysite-metahalloysite in those older than 2000-6000 yrs. Therefore, the time needed for weathering should be considered as an important factor.

As shown in Table 6 and Fig. 21, such conclusion is also held by the studies on weathering of the volcanic ashes in Hokkaido (SASAKI and ISHIZUKA, 1956, ISHII and SASAKI, 1959; KANNO, 1959 a; MIYAZAWA, 1966).

Unequal rates of the crystallization process, however, may be caused by either the mechanical composition of the deposit itself or the intensity of weathering. Such difference among the pyroclastic deposits was found in the Nemuro district in the eastern part of Hokkaido (ISHII and KONDŌ, 1962 a, b; ISHII, 1963). In this district the degree of weathering does not always depend on an increase in depth. As shown in Fig. 20, the samples from the Mf pumice-flow deposit ($6460 \pm 130-7190 \pm 230$ yrs. B.P.) and the Ml pumice-fall deposit (older than 8000 yrs.) are in the allophanic stage, while the sample from the Mk ash-fall deposit which lies between the above two deposits, proceeds to the halloysite stage. The Ml pumice-fall deposit consists of coarse pumice lumps, while the Mk ash-fall deposit which accumulated on the former, is composed of very fine volcanic ash. The Mk and Ml deposits show no considerable difference in the time interval exposing on the surface. This fact suggests that a process from allophane to halloysite is determined not only by the time factor but also by the grain-size of the parent material.

Occurrence of the 2:1 type clay minerals is confined within the certain volcanic districts. As mentioned in the preceding chapter, the pyroclastic deposits in which the 2:1 type clay minerals like montmorillonite are dominant is so far restricted within the circumference of the Usu volcano. Montmorillonite, 14 Å minerals and illite as an accessory component can be rarely found in the pyroclastic deposits in the Oshima Peninsula and a part of the northernmost Hokkaido (KONDŌ, 1967; Jūnenchi Group, 1967; SASAKI *et al.*, 1967) (Fig. 21). The recent mafic pyroclastics in the Usu volcanic district show an extraordinary weathering, as mentioned before. In this case, under the subsurface condition with weakly alkaline ($\text{pH}=7.5-8.0$) environment, mafic glass, olivine and other constituents

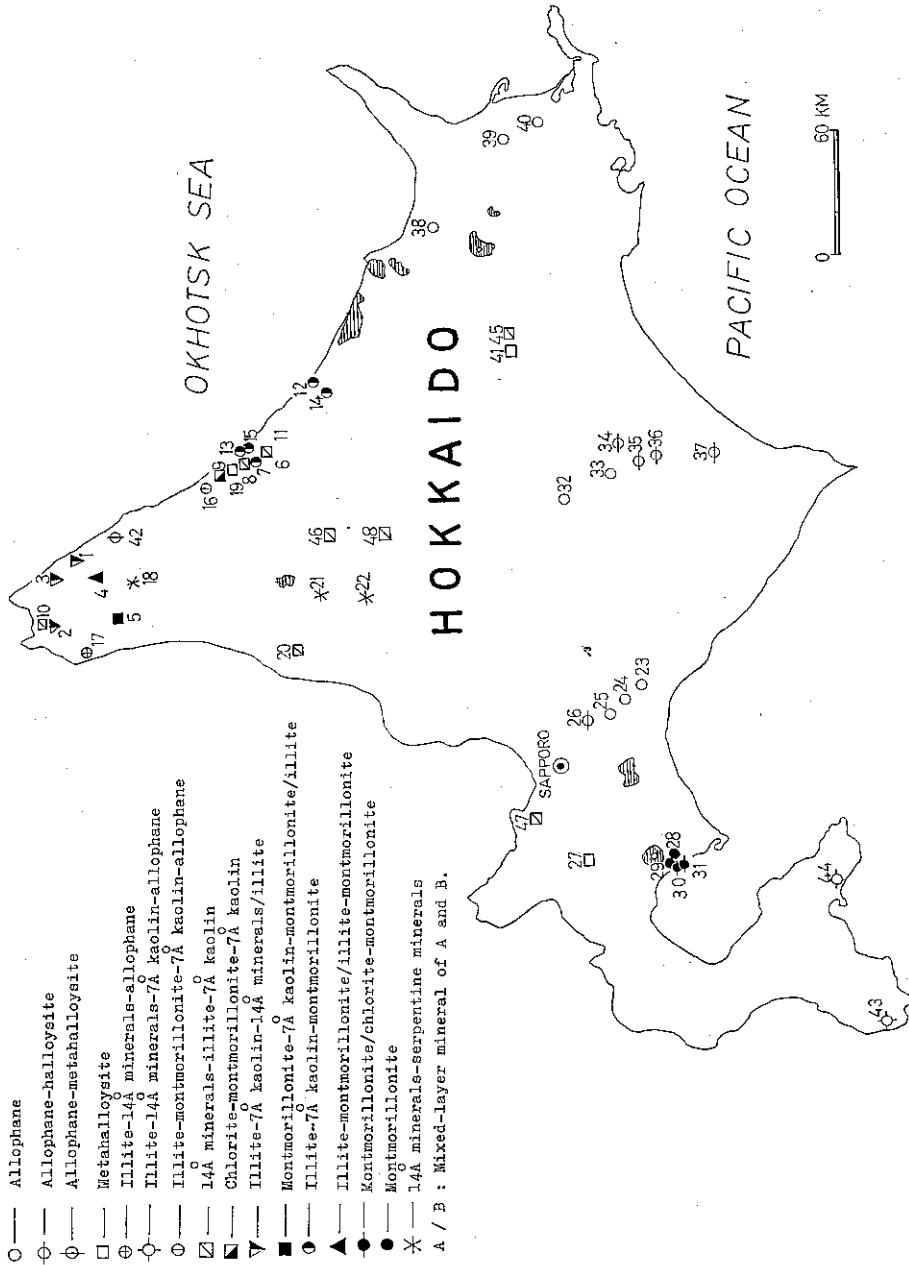


Fig. 21. Clay mineral assemblage of the weathered pyroclastic deposits, and the other rocks.

Table 6. Clay mineral assemblage of the weathered rocks.

No.	Locality	Rocks and sediments	Clay mineral assemblage
1	Nakasarfutsu, Sarufutsu	Unconsolidated sediments	Illite-7 Å kaolin-14 Å mineral/illite
2	Kami-koitōi, Wakkanai	Unconsolidated sediments and sandstone	Illite-7 Å kaolin-14 Å mineral/illite
3	Onishi-betsu, Sarufutsu	Unconsolidated sediments	Illite-7 Å kaolin-14 Å mineral/illite
4	Kami-sarufutsu, Sarufutsu	Siltstone	Illite-montmorillonite/illite-montmorillonite
5	Minami-zawa, Horonobe	Siltstone	Montmorillonite-7 Å kaolin-montmorillonite/illite
6	Chōkai (1), Ōmu	Red weathered crust derived from siltstone	14 Å mineral-illite-7 Å kaolin
7	Sawaki, Okkōpe	Red weathered crust derived from tuffaceous siltstone	Illite-7 Å kaolin-montmorillonite
8	Akebono (1), Ōmu	Unconsolidated sediments (tuffaceous clay)	14 Å mineral-illite-7 Å kaolin
9	Horonai-kawakita, Ōmu	Unconsolidated sediments	Chlorite-montmorillonite-7 Å kaolin
10	Koitōi, Wakkanai	Unconsolidated sediments	14 Å mineral-illite-7 Å kaolin
11	Chōkai (2), Ōmu	Unconsolidated sediments	Illite-7 Å kaolin-montmorillonite
12	Komukai, Monbetsu	Unconsolidated sediments (tuffaceous clay)	Illite-7 Å kaolin-montmorillonite
13	Akebono (2), Ōmu	Unconsolidated sediments (tuffaceous clay)	Illite-7 Å kaolin-montmorillonite
14	Yasoshi, Monbetsu	Unconsolidated sediments (tuffaceous clay)	Illite-7 Å kaolin-montmorillonite
15	Akebono (3), Ōmu	Unconsolidated sediments (tuffaceous clay)	Illite-7 Å kaolin-montmorillonite
16	Fureppu, Esashi	Pyroclastic rock (andesitic ash-fall)	Illite-montmorillonite-7 Å kaolin-allophane
17	Acharu, Toyotomi	Pyroclastic rock (andesitic ash-fall)	Illite-14 Å mineral-allophane
18	Toikanbetsu, Horonobe	Serpentinite	14 Å mineral-serpentine minerals (lizardite, antigorite and chrysotile)
19	Motoineppu, Ōmu	Red weathered crust derived from welded tuff	Halloysite-halloysite/hydrated halloysite
20	Tomamai	Unconsolidated sediments	14 Å mineral-illite-7 Å kaolin
21	Soeshi-nai, Horokanai	Serpentinite	Serpentine minerals (chrysotile and lizardite)
22	Numaushi, Horokanai	Serpentinite	Serpentine minerals (chrysotile and lizardite)
23	Hayakita	Pyroclastic rock (andesitic pumice-fall)	Allophane
24	Bibi, Chitose	Pyroclastic rock (andesitic pumice-fall)	Allophane
25	Chitose	Pyroclastic rock (andesitic pumice-fall)	Allophane
26	Shimamatsu	Pyroclastic rock (andesitic pumice-fall)	Allophane-hydrated halloysite
27	Izumo, Kucchan	Pyroclastic rock (andesitic ash-fall)	Halloysite

No.	Locality	Rocks and sediments	Clay mineral assemblage
28	Shôwa-shinzan, Sôbetsu	Pyroclastic rock (andesitic ash-fall)	Montmorillonite
29	Nishi-kohan, Sôbetsu	Pyroclastic rock (andesitic mud-flow)	Montmorillonite
30	Usu, Date	Pyroclastic rock (andesitic ash-fall)	Montmorillonite/chlorite-montmorillonite
31	Nagawa, Date	Pyroclastic rock (andesitic ash-flow)	Montmorillonite/chlorite-montmorillonite
32	Shintoku	Pyroclastic rock (andesitic ash-fall)	Allophane
33	Memuro	Pyroclastic rock (andesitic ash-fall)	Allophane
34	Obihiro	Pyroclastic rock (andesitic ash-fall)	Allophane-hydrated halloysite
35	Kawanishi, Obihiro	Pyroclastic rock (andesitic ash-fall)	Allophane-hydrated halloysite
36	Taishô, Obihiro	Pyroclastic rock (andesitic ash-fall)	Allophane-hydrated halloysite
37	Taiki	Pyroclastic rock (andesitic ash-fall)	Allophane-hydrated halloysite
38	Koshimizu	Pyroclastic rock (andesitic pumice-fall)	Allophane
39	Naka-shibetsu	Pyroclastic rock (andesitic ash-fall)	Allophane
40	Nishibetsu, Bekkai	Pyroclastic rock (andesitic pumice-flow & dacitic pumice-fall)	Allophane
41	Rikubetsu	Mafic andesite	Halloysite-halloysite/hydrated halloysite
42	Hama-tonbetsu	Pyroclastic rock (andesitic ash-fall)	Allophane-halloysite
43	Shizuura, Matsumai	Pyroclastic rock (andesitic ash-fall)	14 Å mineral-illite-7 Å kaolin-allophane
44	Asahioka, Hakodate	Pyroclastic rock (andesitic ash-fall)	Illite-14 Å mineral-7 Å kaolin-allophane
45	Shôtoshibetsu, Rikubetsu	Pyroclastic rock and quartzite	Illite-14 Å mineral (vermiculite)-7 Å kaolin
46	Shigashitayoro, Shibetsu	Red weathered crust derived from unconsolidated sediments	Illite-14 Å mineral (vermiculite)-7 Å kaolin
47	Otaru	Red weathered crust derived from agglomerate	Illite-14 Å mineral (vermiculite)-7 Å kaolin
48	Bibakaraushi, Kenbuchi	Red weathered crust derived from agglomerate	Illite-14 Å mineral (vermiculite)-7 Å kaolin

Numbers of each localities same as in Fig. 21.

Mineral analysts. 12: UCHIYAMA and SHÔJI (1964); KONDÔ (1967 a); 21, 22: SASAKI *et al.* (1965); 23, 24, 25, 26: ISHII and KONDÔ (1962 a, b); 27: MIYAZAWA (1966); 32: ISHII and KONDÔ (1962 a, b); 33: MIYAZAWA (1966); 34, 35: ISHII and KONDÔ (1962 a, b); 36: SASAKI and ISHIZUKA (1956 b); 37: ISHII and SASAKI (1959); 38: MIYAZAWA (1966); 43, 44: SASAKI *et al.* (1967); 45, 46, 47, 48: YANO (1967); The mineral analyses of all other number samples were performed by the author himself.

a/b: Mixed-layer mineral of a and b.

have altered to mixed-layer mineral of montmorillonite-chlorite through iron-rich montmorillonite and illite. However, even in the case of the weathering of mafic pyroclastics, an alteration process to kaolinitic clay through the allophanic stage was taken place under the surface condition with severe leaching.

In addition to allophane and kaolin minerals, the 2:1 type clay minerals may be found in the weathered pyroclastics of the other districts in Hokkaido. A soil from the 1866 volcanic ash erupted from the Lake Rotomahana, New Zealand, contains montmorillonite. It is probable that this material has been hydrothermally altered prior to eruption, because montmorillonite was found in the hydrothermally altered pumiceous sands (GRANWELL and BIRRELL, 1954). Montmorillonite is also found in a soil from the dacitic ash at Kawatabi, Miyagi Prefecture (UCHIYAMA *et al.*, 1961). JENNE (1961) has reported montmorillonite as well as amorphous colloids in coastal soils of Oregon which show morphological and chemical features of volcanic ash soils elsewhere. It is noticed here that the montmorillonites from Kawatabi and Oregon represent the H or Al form in which exchangeable cations were leached.

KANNO *et al.* (1959 b, 1961 a) have reported that the 1959 volcanic ash erupted from the Shimmoe-dake of the Kirishima volcanic group is of secondary origin. According to them, the clay fractions of the 1959 ash are rich in beidellite, chlorite, and vermiculite, mostly interstratified each other. These montmorillonite and 14 Å minerals are considered to have been formed before the eruption under the reduced condition at the bottom of the crater lake.

Very recently, MASUI and SHÔJI (1967) have reported montmorillonite, intergrade of vermiculite and Al-chlorite as well as allophane and 7 Å kaolin mineral in volcanic ash soils in the Tôhoku and Hokkaido. A paragenesis of expanding 14 Å minerals (mainly Al-vermiculite) and allophane has also been reported in the weathered volcanic ashes in central Japan (MATSUI, 1960; KURAHAYASHI and TSUCHIYA, 1965).

According to GRIM (1958), volcanic ashes rich in magnesium tend to form montmorillonite, but those poor in this element allophane and kaolin minerals. Formation of montmorillonite is not expected by means of mere weathering from the surface, but it is possible in a deeper place where alteration advances without sufficient supply of oxygen (MORIMOTO and OSSAKA, 1964).

Recently, the syntheses of layer-silicates have been carried out at low temperatures and normal pressures with the production of various proportions of gels and crystalline phases (KIMPE, GASTUCHE and BRINDLY, 1961). It is shown that the properties of the gels influence the kind of crystals synthesized. The main factors in relation to clay mineral formation are pH, salt concentration, and the (Al or Mg)/SiO₂ ratio. Kaolinite has been synthesized at low pH's (4.2-6.5) and mica-like minerals at higher pH's (6.5-9.0). Serpentine minerals have been obtained in an intermediate pH range. The better yield of magnesium-bearing minerals may be attributed to the six-fold coordination of this cation. These synthetic

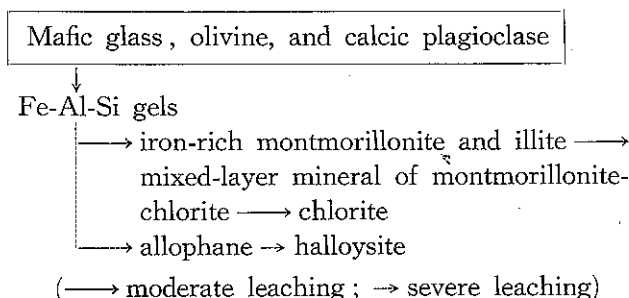
experiments suggest that various clay minerals are formed depending on the type of cation involved and the pH of the solution.

The complicated paragenesis of the 2:1 type and 1:1 type clay minerals derived from the weathered pyroclastics is still not proved in detail.

CHAPTER 6. CONCLUSIONS

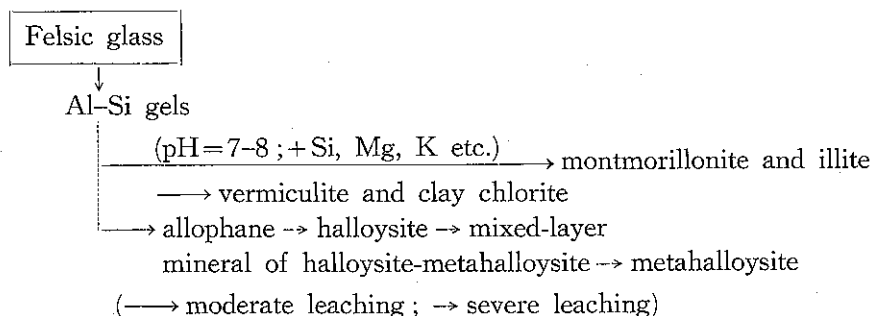
Clay-mineralogical study on the pyroclastic deposits in the Usu volcanic district was made in order to research their weathering process. On the basis of geological and tephrochronological studies, about 20 samples ($< 2 \mu$ clay fractions) were separated from the weathered pyroclastic materials and examined by the aid of X-ray diffraction, differential thermogram, infra-red spectra, electron microscopy, and chemical analysis.

Two different processes of weathering are found in the Usu pyroclastic deposits mostly composed of mafic materials; one is the formation of iron-rich montmorillonite and the other is that of kaolinitic type clay, as shown in the following relation:



In this case, the 2:1 type clay minerals are predominant. They are considered to have formed under the alkaline and wet conditions at the deeper level from the surface. It is noticed that the recent Usu pyroclastics, especially historic ones, have been already altered under such conditions prior to eruption, forming the 2:1 type clay minerals. Even from the mafic parent material a small amount of the 1:1 type clay mineral may be produced at the surface where intense leaching prevails.

Similar two processes are also recognized in the weathering of the older felsic pyroclastic deposits in this district, as shown in the following:



It has been generally accepted that weathering process of felsic pyroclastics in Hokkaido and other regions commonly proceeds toward metahalloysite through allophane and halloysite. Such type of weathering is also found in this district. However, the most characteristic feature of weathering process in this district is the formation of the 2:1 type clay minerals which seem to have been produced under the high pH condition with simultaneous addition of silica, magnesium and alkalis from the overlying deposits.

In view of the above results together with those in Japan and other regions and those of synthetic experiments of clay mineral, it may be concluded that the main factors in determining the paragenesis of clay minerals formed through weathering are a) physical properties of deposit (mainly permeability), b) chemical composition of parent material, c) concentration of bases and alkalis, d) prevailing pH, e) ratio of aluminum to silica, f) oxidation-reduction potential (Eh) of weathering solution and g) time interval of weathering. Further studies will be needed with regard to the rôle and mechanism of these factors.

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References

- 1) AOMINE, S. and WADA, K. (1962): Differential weathering of volcanic ash and pumice, resulting in formation of hydrated halloysite. *Amer. Mineral.*, **47**, 1024-1048.
- 2) BATES, T. F. (1958): Selected electron micrographs of clays and other fine-grained minerals. *Coll., Mineral Ind., Pen. State Univ., Cir.* **51**, Pennsylvania.
- BATES, T. F. (1962): Halloysite and gibbsite formation in Hawaii. *Clays and Clay Minerals*, **11**, 315-328.

- 3) BESOAIN, E. (1964): Volcanic ash soils of Chile. *Meeting on the classification and correlation of soils from volcanic ash, World Soil Resources Reports 14*, 92-93, FAO/UNESCO, Rome.
- 4) BROWN, G. (Editor) (1961): The X-ray identification and crystal structures of clay minerals. *Mineralogical Society, London*.
- 5) FIELDER, M. and SWINDALE, L. D. (1954): Chemical weathering of silicates in soil formation. *New Zealand J. Sci. Tech.*, **B**, 36, 140-150.
 FIELDER, M. and SWINDALE, L. D. (1955 a): Clay mineralogy of New Zealand soils. Part 1: Electron micrography. *New Zealand J. Sci. Tech.*, **B**, 37, 314-335.
 FIELDER, M. and SWINDALE, L. D. (1955 b): Clay mineralogy of New Zealand soils. Part 2: Allophane and related mineral colloids. *New Zealand J. Sci. Tech.*, **B**, 37, 336-350.
- 6) FUKUTOMI, K. and ISHIKAWA, T. (1944): Crustal movement caused on Usu volcano in 1944. *Bull. Seism. Soc. Japan*, **16**, 214-224, 242-249, 263-270.
- 7) GOLDICH, S. S. (1938): A study in rock weathering. *J. Geol.*, **46**, 17-58.
- 8) GRANWELL, M. and BIRRELL, K. S. (1954): Physical properties of certain volcanic clays. *New Zealand J. Sci. Tech.*, **B**, 36, 108-122.
- 9) GRIM, R. E. (1958): Concept of diagenesis in argillaceous sediments. *Bull. Amer. Assn. Pet. Geol.*, **42**, 246-253.
- 10) HARRISON, J. B. (1933): The katamorphism of igneous rocks under humid tropical conditions. *Imp. Bureau of Soil Sci., Rothamsted Expt. Sta., Harpenden, England*.
- 11) ISHII, J. and SASAKI, T. (1959): On the clay minerals of clayey loam in the Tokachi district, Hokkaido. *Bull. Geol. Com. Hokkaido*, **38**, 13-21.
 ISHII, J. and KONDÔ, Y. (1962 a): Clay minerals of Quaternary volcanic ash and pumice deposits in Hokkaido. *Earth Sci.*, No. **62**, 29-45.
 ISHII, J. and KONDÔ, Y. (1962 b): Clay minerals of Quaternary volcanic ash and pumice deposits in Hokkaido. *Advances in clay Sci.* (4), 193-212.
 ISHII, J. (1963): The weathering processes of volcanic ash and pumice deposits in Hokkaido. *J. Fac. Sci. Hokkaido Univ. Ser. IV*, **11**, 545-569.
- 12) ISHIKAWA, T. (1950): New eruption of Usu volcano. *Science and scientific education*. No. **1**, 18-23.
 ISHIKAWA, T. (1950): New eruption of Usu volcano, Hokkaido, Japan during 1943-1945. *J. Fac. Sci. Hokkaido Univ., Ser. IV*, **7**, 237-260.
- 13) JENNE, E. A. (1961): Mineralogical, chemical, and fertility relationships of five Oregon coastal soils. *Ph. D. thesis, Oregon State College*.
- 14) Jûnenchi Group (1967): Soils in northern Hokkaido, Japan. *Hokkaido Development Agency, Sapporo*.
- 15) KANNO, I. (1959 a): Clay minerals of volcanic ash soils and pumices from Japan. *Advances in Clay Sci.* (1), 213-233.
 KANNO, I. ARIMURA, S. and KUWANO, Y. (1959 b): Sulfur compounds in the Simmoe ash of the Kirishima Volcanic Cluster, erupted on February 17, 1959. *Pedologist*, **3**, 50-53
 KANNO, I., HONJÔ, Y. and KUWANO, Y. (1961 a): Clay minerals of volcanic ash erupted from the Shimmoë-dake of the Kirishima Volcanic Cluster on February 17, 1959. *Advances in Clay Sci.* (3), 214-224.
 KANNO, I. (1961 b): Genesis and classification of main genetic soil types in Japan (Pt. 1). *Bull. Kyushu Agr. Expt. Sta.*, **7**, 1-185.
- 16) KATSUI, Y. (1962): Petrochemistry of the Quaternary volcanic rocks of Hokkaido. *J. Fac. Sci. Hokkaido Univ., Ser. IV*, **11**, 1-58.

- 17) KELLER, W. D. (1957): The principles of chemical weathering *Lucas Brothers Publishers, Columbia, Missouri.*
- 18) KIMPE, C. D., GASTUCHE, M. C. and BRINDLEY, G. W. (1961): Ionic coordination in aluminosilicic gels in relation to clay mineral formation. *Amer. Mineral.*, **46**, 1370-1381.
- 19) KONDÔ, Y. (1962): Clay mineralogical study on Quaternary pyroclastic deposits of the Usu volcanic district. *Master thesis, Dept. Geol. Min., Hokkaido Univ.*
 KONDÔ, Y. (1963): Clay mineralogical study on Quaternary pyroclastic deposits of the Usu volcanic district, Hokkaido. *J. Geol. Soc. Japan*, **69**, 362-377.
 KONDÔ, Y. (1965): Clay minerals of Quaternary volcanic ash and pumice deposits in Hokkaido (2nd Report). *Advances in Clay Sci.* (5), 1-18.
 KONDÔ, Y. (1967): Clay mineral compositions of the Quaternary pyroclastic deposits and the soils in Hokkaido, Japan. *Hokkaido Development Agency, Sapporo.*
- 20) KURAHAYASHI, S. and TSUCHIYA, T. (1965): The clay mineralogical study of the Kanto Loam Formation (4). *Advances in Clay Sci.* (5), 19-32.
- 21) MARSHALL, C. E., HUMBERT, R. P., SHAW, B. T. and CAIDWELL, O. G. (1942): Studies of clay particles with the electron microscope: 2, *Soil Sci.*, **54**, 149-158.
- 22) MATSUI, J. and SHÔJI, S. (1967): Some problems on clay minerals of volcanic ash soils. *Pedologist*, **11**, 33-45.
- 23) MATSUI, T. (1960): On clay minerals in recent soil and palaeosol derived from the Pleistocene volcanic ash near Utsunomiya. *Advances in Clay Sci.* (2), 229-241.
- 24) MIMATSU, M. (1962): Diary of the growth of Shôwa-Shinzan. *Private-press, Sapporo.*
- 25) MINAKAMI, T. (1944): On the activities of Usu volcano. *Prel. Rept. Earthq. Res. Inst., Tokyo Univ.*, **3**, 1-22.
 MINAKAMI, T. (1947): Recent activities of volcano Usu. *Bull. Earthq. Res. Inst.* **25**, 1-4, 65-67.
 MINAKAMI, T., ISHIKAWA, T. and YAGI, K. (1951): The 1944 eruption of volcano Usu in Hokkaido, Japan. *Bull. Volcanologique, Ser. 2, Tom. 11*, 45-157.
- 26) MINATO, M. (1966): ¹⁴C age of the Toya ash flow II. *Earth Sci.*, **No. 82**, 42-43.
- 27) MIYAZAWA, K. (1966): Clay mineral composition of Andosols in Japan. *Bull. Nat. Inst. Agr. Sci. Ser. B*, **No. 17**, 1-100.
- 28) MORIMOTO, R. and OSSAKA, J. (1964): Low temperature mud-explosion of Mt. Yake, Prefs. Nagano-Gifu, central Japan, on 17th June 1962, as an example of endogeneous Katamorphism of volcanic rock at the destructive stage of the volcano. *Bull. Volcanologique*, **27**, 3-4.
- 29) NAGANUMA, Y., URAGAMI, K. and TOGASHI, R. (1933): Investigation on the volcanic ashes in Hokkaido, II. On the distribution of volcanic ashes in the central part of the Iburi district, Hokkaido. *Bull. Volc. Soc. Japan*, **1**, 81-94.
- 30) ÔBA, Y., and KONDÔ, Y. (1964): Pumice-fall deposit of Usu volcano, Hokkaido. *Bull. Volc. Soc. Japan, Ser. 2*, **9**, 73-86.
- 31) ÔBA, Y. (1966): Geology and petrology of Usu volcano, Hokkaido, Japan. *J. Fac. Sci. Hokkaido Univ., Ser. IV*, **13**, 185-236.
- 32) OINUMA K., KOBAYASHI, K. and SUDÔ, T. (1961): Procedure of clay mineral analysis. *Clay Sci.*, **1**, 23-28.
- 33) ÔMORI, F. (1911): The Usu-san eruption and earthquake and elevation phenomena. *Bull. Imp. Earthq. Inv. Com.*, **1**, 1-38.
- 34) OSSAKA, J. (1960): On the hydro-alumina silicate minerals from Mt. Asama. *Advances in Clay Sci.* (2), 339-349.

- 35) ÔTA, R. (1956): Explanatory text of the geological map of "Abuta" (scale 1:50,000). *Geol. Surv. Japan*.
- 36) POLYNOV, B. B. (1937): The cycle weathering. Translated by Muir, A., London.
- 37) RICH, C. I. and KUNZE, G. W. (Editor) (1964): Soil clay mineralogy. *The Univ. of North Carolina Press, Durham, North Carolina*.
- 38) ROSS, C. S. and HENDRICKS, S. B. (1945): Minerals of the montmorillonite group. *U. S. Geol. Survey Prof. Paper, 205 B*, 60-64.
- 39) SASAKI, S. and ISHIZUKA, Y. (1956): On the volcanic ash soil in Tokachi district, Hokkaido island. *J. Sci. Soil and Manure, Japan*, **27**, 135-139.
SASAKI, S., MATSUNO, T. and YAZAWA, T. (1967): On the clay minerals of the Kuroboku soil in Hokkaido. (unpublished).
- 40) SATŌ, D. (1913): Preliminary report on the explosion of Usu volcano. *Bull. Geol. Surv. Japan*, **22**, 1-46.
- 41) SAWHNEY, B. L. (1959): Aluminium interlayer in soil minerals, montmorillonite and vermiculite. *Nature*, **18**, 1595-96.
- 42) SERRATOSA, J. M. (1962): Dehydration and rehydration studies of clay minerals by infra-red absorption spectra. *Clays and Clay minerals*, **11**, 412-418.
- 43) SHERMAN, C. D. and UEHARA, G. (1956): The weathering olivine basalt in Hawaii and its pedogenic significance. *Soil Sci. Soc. Amer. Proc.*, **20**, 337-340.
- 44) STUBIČAN, V. and ROY, R. (1961 a): Isomorphous substitution and infra-red spectra of the layer lattice silicates. *Amer. Mineral.*, **46**, 32-51.
STUBIČAN, V. and ROY, R. (1961 b): A new approach to assignment of infra-red absorption bands in layer-structure silicates. *Zeit. Krist.*, **115**, 200-214.
- 45) SUDŌ, T. (1959): Mineralogical study on clays of Japan. *Maruzen, Tokyo*.
- 46) SWINDALE, L. D. (1966): A mineralogical study of soils derived from basic and ultrabasic rocks in New Zealand. *New Zealand J. Sci.*, **9**, 484-506.
- 47) TAMURA, T. (1958): Identification of clay minerals from acid soils. *J. Soil Sci.*, **9**, 141-147.
- 48) TSUCHIYA, T. and KURAHAYASHI, S. (1958): On the clay minerals of the Kanto Loam. *J. Geol. Soc. Japan*, **64**, 605-615.
TSUCHIYA, T. and KURAHAYASHI, S. (1959): Clay mineralogical studies on the Kanto Loam. *Advances in Clay Sci. (1)*, 113-120.
- 49) UCHIYAMA, N. *et al.* (1962): Montmorillonite in a volcanic ash soil. *Soil Sci. and Plant Nutrition*, **8**, 13-19.
UCHIYAMA, N. and SHŌJI, S. (1964): Clay minerals of a diluvial soils in Hokkaido. *Tohoku J. Agr. Res.*, **15**, 131-145.
- 50) WALKER, G. F. (1958): Reaction of expanding-lattice clay minerals with glycerol and ethylene glycol. *Clay Mineral Bull.*, **3**, 302-313.
- 51) WIEDEN, P. (1960): Ein eisenarmer Nontronite. *Tschermaks Mineralogische und Petrographische Mitteilungen*, **7**, 194.
- 52) YAGI, K. (1949): Petrological studies on Shōwa-Shinzan, Usu volcano, Hokkaido, Japan. *J. Jap. Assoc. Min. Peter. Econ. Geol.*, **33**, 3-17.
YAGI, K. (1953): Recent activity of Usu volcano, Japan, with special reference to formation of Shōwa-Shinzan. *Transact. Amer. Geophys. Union*, **33**, 447-456.
- 53) YAMADA, S. (1958): Studies on the history of volcanic eruptions of alluvium epoch in Hokkaido on the basis of depositional features of the pyroclastics. *Mono. Assoc. Geol. Coll.*, **No. 8**, 1-40.

- YAMADA, S., KATSUI, Y. and KONDÔ, Y. (1963): Distribution and chronology of the Quaternary pyroclastic deposits in Hokkaido. *Quat. Res.*, 3, 80-87.
- 54) YANO, Y. (1967): On the red soils in Hokkaido. (unpublished).

摘 要

岩石および堆積物の風化過程に関する研究は、今日では地質学、鉱物学、土壌学および地球化学の分野における共通の研究課題となっている。風化過程の本質を究明するためには、気候条件を異にする各地域において、岩石および堆積物の地質年代、岩質、構成鉱物などの性状を明らかにし、風化の初期段階からの詳細な化学的、鉱物学的研究が必要である。最近、風化過程の研究においては、風化作用により生成された粘土の鉱物学的研究が重要視され、粘土鉱物組成およびその変化の追究が、風化過程の指標としてきわめて有効であることが確認されてきた。

この論文は、西南北海道の有珠火山地域における第四紀火山碎屑物の風化過程について、主に化学的風化作用と粘土鉱物の生成・変化の関係を中心に究明したものである。さらに北海道に広く分布する第四紀火山碎屑物の風化過程についても、既往の著者ならびに他の研究者の業績を比較参照しつつ、珪長質火山ガラスを主体とする軽石質火山灰の粘土鉱物化について論及している。

まず、有珠火山地域の火山碎屑物につき、火山灰編年学を基礎にして詳細な地質調査をおこない、碎屑物の年代、岩質、噴出機構および堆積様式を明らかにし、分析試料の取り扱い方に火山学的な考慮をはらっている。上部洪積世から現在にいたる風化火山碎屑物の代表的なもの 18 試料につき、一般化学性が明らかにされ、 2μ 以下の粘土部分につき X 線回析、示差熱分析、赤外線吸収スペクトル、化学分析および電子顕微鏡観察を併用して、構成粘土鉱物の種類と性質が決定されている。これらの資料にもとづき、有珠火山地域の火山碎屑物の風化過程の様式が詳論されている。

以上の結果と、これまでの研究資料をもとに、北海道の第四紀火山碎屑物の風化過程に関する一般的様式を求めた。

以上の研究結果は、次のように要約することができる。

(1) 有珠火山地域における沖積世の苦鉄質火山碎屑物は、堆積環境の差異により 2, 3 の特異な風化過程を示す。すなわち、苦鉄質碎屑物が風化の初期において、より新期の火山噴出物に被覆されたり、火口原あるいは火口湖のような閉鎖された堆積環境にあっては、脱珪酸、脱塩基作用が緩慢なため、苦鉄質火山ガラス、カンラン石などは弱アルカリ反応 ($\text{pH}=7.5\sim 8.0$) の下で分解が進行する。この過程で、含水シリカ・アルミナ・鉄のゲル状物質は、アルカリ、塩基と結合し、主として鉄に富むモンモリロナイト鉱物を生成する。また火口原あるいは火口湖においては、上記粘土鉱物のほかイライト、およびモンモリロナイトとリョクデイ石の混合

層鉱物をも生成する。このような場合、生成粘土は $\text{SiO}_2/\text{Al}_2\text{O}_3$ (モル比) が4以上で高く、 SiO_2 、 Fe_2O_3 、 CaO に富み、かつアルカリにやや富むという特徴をしめす。

しかし、苦鉄質火山碎屑物であっても、永く地表に露出し、脱珪酸、脱塩基作用が著しい場合は、 Al_2O_3 に富む非晶質なアロフェンを主成分とし、低結晶度のカオリン鉱物に変化してゆくものと推定される。

一方、同地域の珪長質な火山碎屑物の風化過程についてみると、従来いわれているようなアロフェンからハロイサイトを主成分とする変化は認められず、堆積環境、とくに水分環境の変化や、上部堆積物からの化学成分の再添加などにより、複雑な粘土鉱物組成をしめすことが明らかにされた。すなわち、流紋岩質ないし石英安山岩質の火山碎屑物においても、2:1型粘土鉱物であるモンモリロナイト、イライト、パーミキュライト、およびリョクデイ石などが比較的多く生成し、これらの鉱物と低結晶度のカオリン鉱物とが共生している例の多いことを確認した。

(2) 北海道に広く分布する珪長質軽石・火山灰を主体とした火山碎屑物は、透水性が良好なため、脱珪酸、脱塩基作用が進み、弱酸性 ($\text{pH}=6.5\sim 5.0$) の反応下で、珪長質火山ガラスから含水シリカ・アルミナのゲル状物質を生成し、非晶質鉱物のアロフェンを経て、低結晶度のカオリン鉱物であるハロイサイト、またはハロイサイトとメタハロイサイトの不規則混合層鉱物に変化する。このような風化過程をたどる場合、生成粘土は $\text{SiO}_2/\text{Al}_2\text{O}_3$ (モル比) が3~2以下で低く、かつ MgO 、アルカリに極端に乏しい。道内諸地域で認められた上記の一般的過程は、本州および北米・ニュージーランド・チリなどの第四紀火山碎屑物の表層風化過程に近似する。

以上のような珪長質火山ガラスからカオリン鉱物への結晶化系列の進化は、従来、主に風化年代(時間)に依存すると考えられてきた。しかし、時間のほかに母材の粒度組成・透水性、ならびに堆積環境の相異などもこの進化の要因として重要であることが、本研究によって明らかにされた。

以上は第四紀火山碎屑物についての風化過程の研究であるが、最近の米国でおこなわれた常温常圧下での層状珪酸塩の合成実験などを参照して、表層風化過程に附随する粘土鉱物の生成、変化について考察した結果、母材の物理的性質(主に堆積物の透水性)、化学組成、風化溶液の塩類濃度と pH 、 SiO_2 量に対する Al_2O_3 の量比、および酸化還元電位 (Eh) などが粘土鉱物の生成条件として主要なものであることを強調した。

将来の研究課題として、珪長質火山ガラスからの2:1型粘土鉱物および1:1型粘土鉱物の複雑な共生関係をより明らかにすることと、岩石物理性の相異なる固結火山岩および種々の岩石の風化過程と、火山碎屑物の風化過程との比較検討が重要であることを指摘した。

Explanation of Plates

Plate I

- Fig. 1.** Sample from the Shōwa-Shinzan ash-fall deposit (Ua_0) showing the "fluffy" appearance, typical of most montmorillonites. Some montmorillonite particles are characteristically lath-shape (indicated by arrows).
- Fig. 2.** Clay separate from the Usu mud-flow deposit (Ua_3) composed of montmorillonite and mixed-layer mineral of montmorillonite-chlorite.

Plate II

- Fig. 1.** Sample from the Usu mud-flow deposit (Ua_3) consisting of iron-rich montmorillonite. Some montmorillonite particles show characteristically lath and elongated bundle forms (indicated by arrows).
- Fig. 2.** Clay separate from the humic soil derived from the Usu somma scoria-fall deposit including allophanic particles.

Plate III

- Fig. 1.** Iron-rich montmorillonite in the Usu somma scoria-fall deposit.
- Fig. 2.** Clay separate from the river terrace deposit consisted mainly of pyroclastic materials. Montmorillonite and some kaolin minerals are seen.

Plate IV

- Fig. 1.** Clay fraction from the Usu pumice-fall deposit (Uc) consisting of illite, chlorite, and kaolin minerals.
- Fig. 2.** Clay fraction from the Usu pumice-fall deposit (Uc) consisting of montmorillonite, illite, and metahalloysite.

Plate V

- Fig. 1.** Clay separate from the river terrace deposit consisted mainly of pyroclastic materials. Montmorillonite and some kaolin minerals are seen.
- Fig. 2.** Altered plagioclase tuff-breccia (Miocene) consisted of well-crystallized kaolinite.

Plate VI

- Fig. 1.** Tarumai pumice-fall deposit (Td) containing many spherules, typical of most allophanes.
- Fig. 2.** Shikotsu pumice-fall deposit ($Spfa_1$) consisted of the kale-shaped or rounded grains showing a concentric plait appearance of low-crystalline halloysite.

