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# CLAY MINERALS OF A DILUVIAL SOIL IN HOKKAIDO

By

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## Introduction

Though many investigations have been made on the soil clays in Japan, there are not many reports concerning the clays of diluvial soils which are of importance next to the alluvial and volcanic ash soils in agriculture. Most papers point out that there were found kaolinite and halloysite as dominating crystalline clay minerals in volcanic ash and diluvial soils. However, a few recent works show that the main clay minerals of diluvial soils as well as of volcanic ash soils consist of randomly and/or regularly Al-interlayered 2:1 minerals (1, 2, 3, 4).

Hokkaido is the northern island of Japan. The annual mean temperatures of this island are 4° to 9°C; annual precipitations, 600 to 1600 mm; and NS quotients, 750 to 1000. Judging from these climatic conditions, there could develop the grey-brown podzolic soil and brown forest soil. Acidic clayey diluvial soils widely distribute in the island. The purpose of this article is to identify the clay minerals in the Monbetsu diluvial soil taken from the acid brown forest region (5) and to make clear the characteristics of the dominating minerals.

## Materials and Methods

The soil samples named B and C were collected respectively from horizons B and C<sub>1</sub> of the diluvial soil at Komukai, Monbetsu City. Table 1 shows the profile of the soil (6). The soil with slightly bleached horizon A<sub>2</sub> is developed and distributed on the diluvial coastal terrace. The soil is acidic and its texture is of heavy clay. Gleization is seen in the subsoil.

Organic matter was first removed from the samples by treatment with 6 per cent H<sub>2</sub>O<sub>2</sub> and then they were dispersed with NaOH. The fractions of <2.0, 2.0-1.0, 1.0-0.5 and <0.5 μ were collected by the sedimentation and centrifuge methods. Iron oxides were removed from the size-fractionated samples by the hydrosulfite-NaHCO<sub>3</sub> method (7). The dehydroxylation-NaOH method was used

**Table 1.** Profile of Monbetsu diluvial soil.

Horizon	Depth (cm)	Soil color	Soil texture	Hardness	Soil structure	Parent material
A <sub>0</sub>	3	Black	Humus	Loose	Granular	Diluvial deposit mixed with fresh volcanic ash
A <sub>1</sub>	11	Dark brown	Clay	Friable	Granular	
A <sub>2</sub>	9	Grey	Clay	Firm	Granular	
B <sub>1</sub>	10	Light yellowish brown	Clay	Very firm	Prismatic	
B <sub>2</sub>	16	Blue grey (with yellowish brown mottlings)	Clay	Very firm	Prismatic	Diluvial deposit
C <sub>1</sub>	24	Blue grey (with yellowish brown mottlings)	Clay	Very firm	Prismatic	
C <sub>2</sub>	—	Blue grey	Clay	Very firm	.....	

for to remove the amorphous matter, interlayered Al and 1:1 minerals in the samples (8).

The cation exchange capacity was determined by the centrifuge washing method employing Ca as the saturating cation and Na to replace it (9). The mono-interlayer specific surface measurement was made by the glycol desorption method (10). Total elemental analysis was made by the semi-micro method (11). Potassium fixation was determined on the clays which were K-saturated, heated at 300°C for 2 hrs., and then leached with ammonium acetate solution for the removal of exchangeable K.

X-ray diffraction patterns were obtained for oriented specimens prepared by drying Ca- or K-clay suspensions on glass slides. The oriented clays were glycol-solvated by applying the ethylene glycol directly to the slide for the X-ray diffraction. The equipment used for the X-ray diffraction was Geigerflex, Rigaku-Denki Co. Ltd., Tokyo, and was operated at 35 KV-15 MA. Differential thermal analysis was made on the Ca-clays at the increasing rate of 10°C per minute.

### Results and Discussion

Table 2 shows the results of the dehydroxylation-NaOH treatment on the iron-removed  $<2\mu$  fractions and CEC of the clay fractions variously treated. The amounts of residues after the treatment increased with increasing of the preheating temperatures up to 300°C, and decreased at the temperatures above 300°C. The minimum amounts of residues were found in the case of preheating at 500°C (B-5 and C-5). Under this condition, not only amorphous matter but also 1:1 minerals and interlayer-Al were considered to be dissolved (8). Both B-5 and C-5 showed that almost half of the samples were dissolved.

Comparing with the results of NaOH treatment without preheating, there was noted a considerable increase in the undissolved matter by the NaOH treatment

Table 2. The amounts of the undissolved after dehydroxylation-NaOH treatment and cation exchange capacity (CEC).

No. of samples	Preheating temperatures (°C)	The amounts of the undissolved after NaOH treatment(%)	CEC (me/100g)
B-0	None	65.5	46.1
C-0	None	62.2	47.1
B-1	110	70.8	45.1
C-1	110	72.5	40.4
B-3	300	77.0	45.4
C-3	300	75.8	40.9
B-4	400	69.1	50.9
C-4	400	67.6	49.7
B-5	500	55.9	77.8
C-5	500	54.3	72.5
B-N*		100.0	35.9
C-N*		100.0	33.6

\* : Original  $<2 \mu$  samples which were only iron-removed.

with preheating at the temperatures below 500°C. As it is reasonably considered that preheating below 500°C does not influence the solubility of crystalline clays, it may be interpreted that the amorphous components changed to the insoluble forms by the preheating.

An increase in CEC after NaOH treatment with preheating seems to be dependent on the dissolution of the amorphous substance and 1:1 minerals. When the preheating temperatures were below 400°C, CEC varied with the amounts of amorphous matter removed. The increase in CEC of the 400°C/NaOH might be largely due to the removal of interlayered Al. The increase of CEC of the 500°C/NaOH may be interpreted to be produced by the destruction of 1:1 minerals.

The X-ray diffraction patterns of Ca-clays after dehydroxylation-NaOH treatment are indicated in Figs. 1 and 2. Both B-N and C-N from which only iron oxides were removed showed broad, and poor diffraction patterns between the peaks 7 and 15Å.

However, extraordinary intensifying of 15.2 Å and 7 Å peaks and lowering of 10.2 Å peak were produced by the NaOH treatment even without preheating. The peaks of 7 Å with shoulder toward 10 Å tend to become sharper with progressively increased temperatures and to disappear after the 500°C/NaOH treatment as seen in B-5 and C-5. Therefore, the peaks at 7 Å and between 7 and 10 Å are presumed to be the (001) diffraction of halloysite and partially hydrated halloysites (8). Though the identification of the clay minerals of B and C clays is made afterwards, here, it can be pointed out that 15.2, 10.2, 7.3, 5.0, 4.27, 3.59 and 3.35 Å peaks can be seen and the poor X-ray diffraction patterns of B-N and C-N may be due to the disturbance by the amorphous matter.

The size-fractionated samples were only NaOH-treated and used for observation by the electron microscope. The pictures of  $<0.5 \mu$  (B-11 and C-11), 0.5-1.0  $\mu$

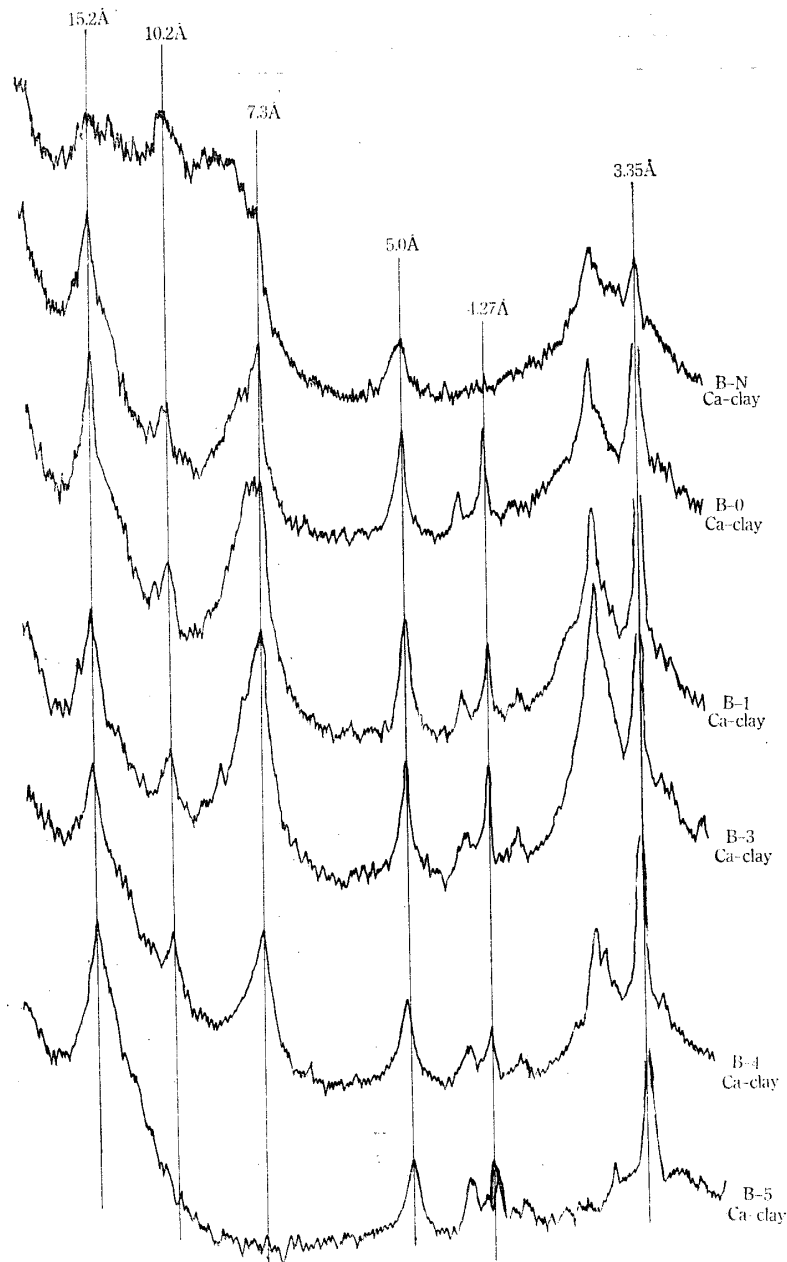


Fig. 1. X-ray diffraction patterns of  $< 2 \mu$  fractions of B horizon after dehydroxylation-NaOH treatment.

(B-12 and C-12) 1.0-2.0  $\mu$  fractions (B-13 and C-13) are presented in Fig. 3. Most crystals were platy and irregular in shape and rather thick being about one tenth of the width. Their sizes ranged from about 5 to 0.02  $\mu$ . There could rarely be seen rod-like halloysite.

Since the platy structure of the crystals such as that at the central part of B-13 in Fig. 3 can be seen, it seems that many thin plates are piled up in the crystals. The shape of the crystals in these pictures are different from those of the typical montmorillonite such as Upton, Wyoming (12) and rather resemble

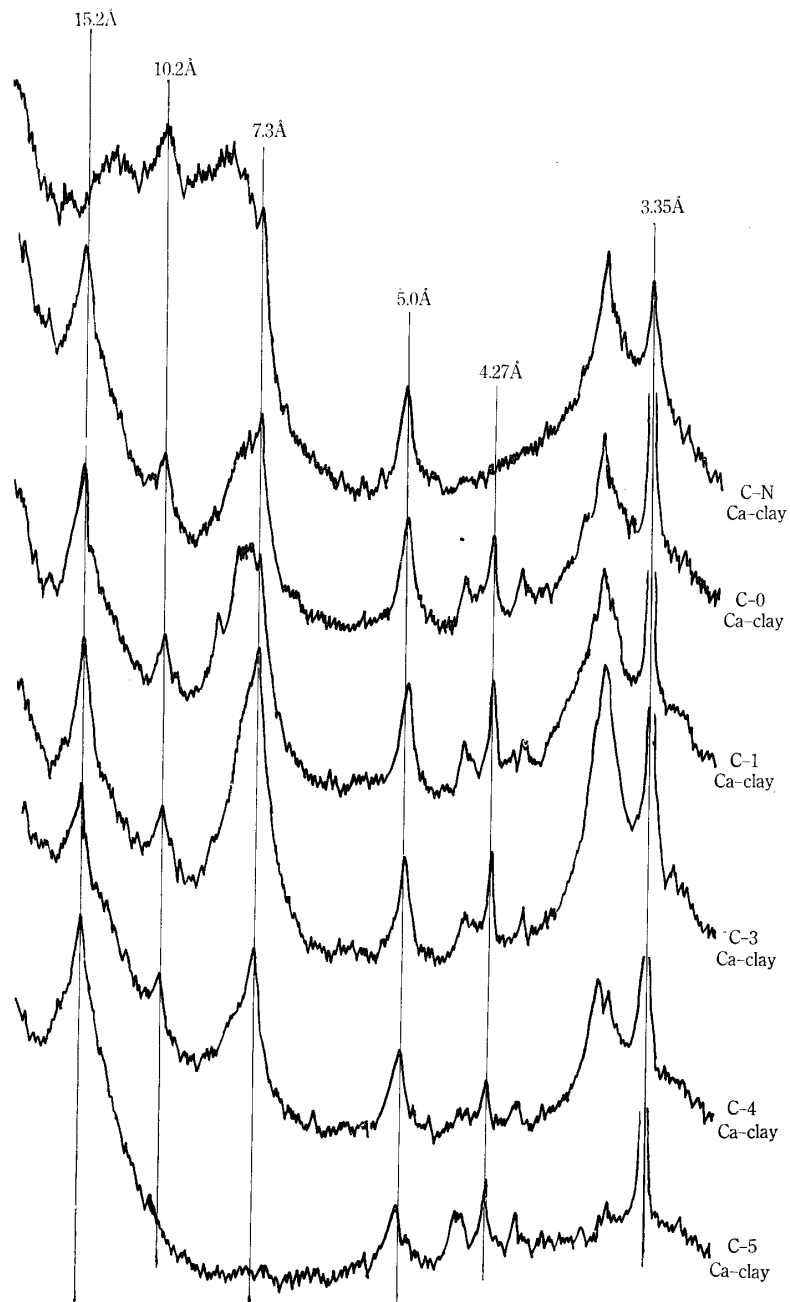


Fig. 2. X-ray diffraction patterns of  $< 2 \mu$  fractions of C horizon after dehydroxylation-NaOH treatment.

to those of illites such as Fithian, Ill. (12) which have clear hems.

The X-ray diffraction patterns of Ca- and ethylene glycol solvated clays of B-11, B-12, B-13, C-11, C-12 and C-13 are given in Figs. 4 and 5. The peaks of 15.2, 10.2, 7.3, 5.0, 4.27, 3.59 and 3.35 Å were observed in all the Ca-clays. However, the 15.2, 10.2 and 7.3 Å peaks are smaller and broader in the finer fractions (B-11 and C-11) than in the coarser fractions. In the finer fractions, the 4.27 and 3.35 Å peaks of quartz are entirely absent.

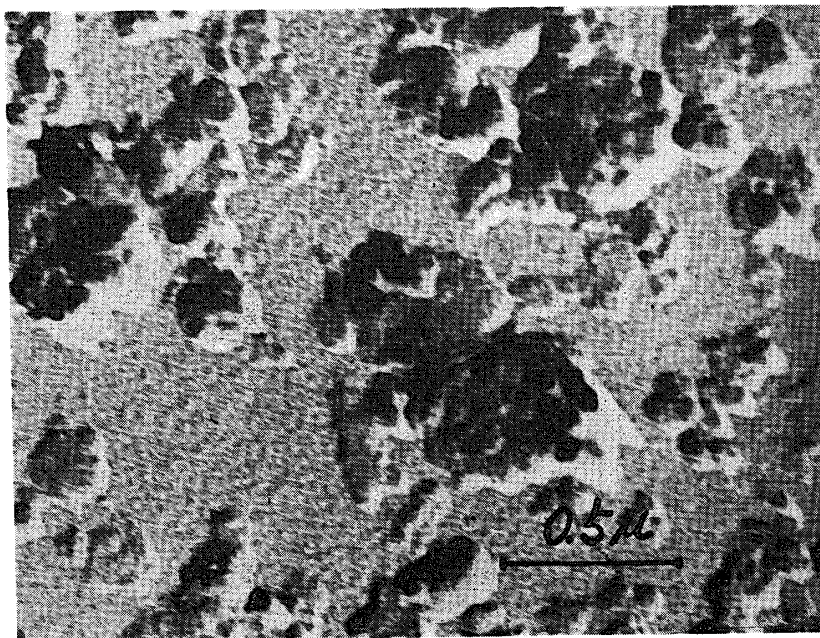
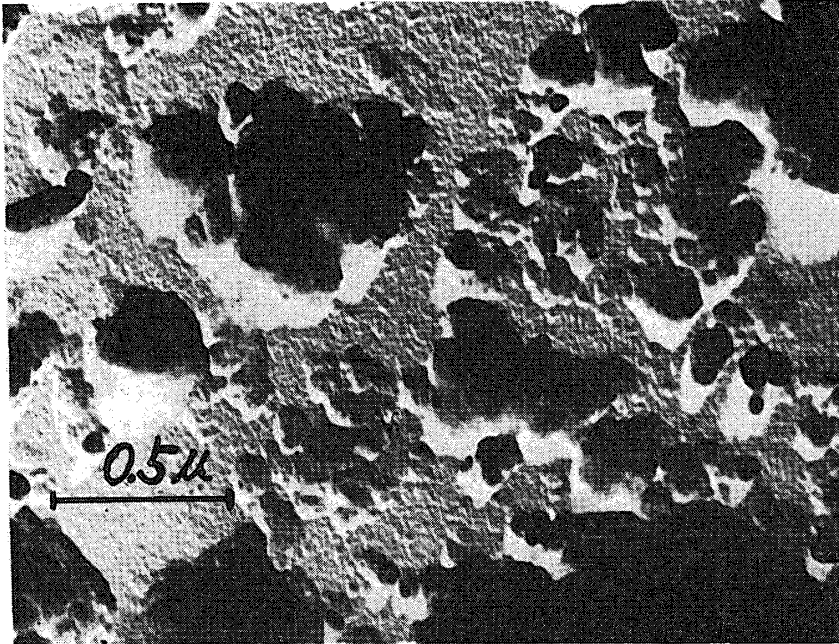


Fig. 3-A. Electron-micrographs of B-11 (upper) and C-11 (lower) after NaOH-treatment.

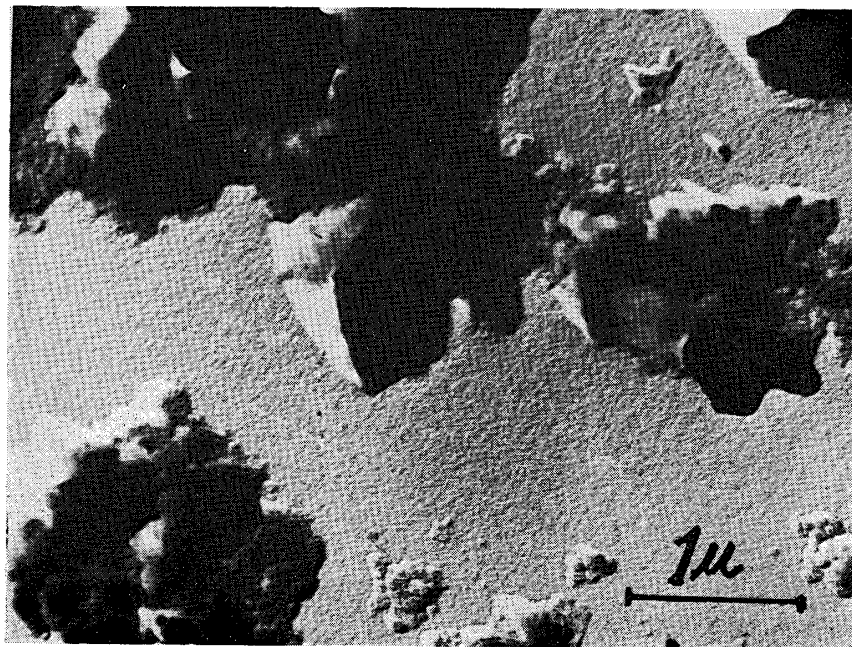
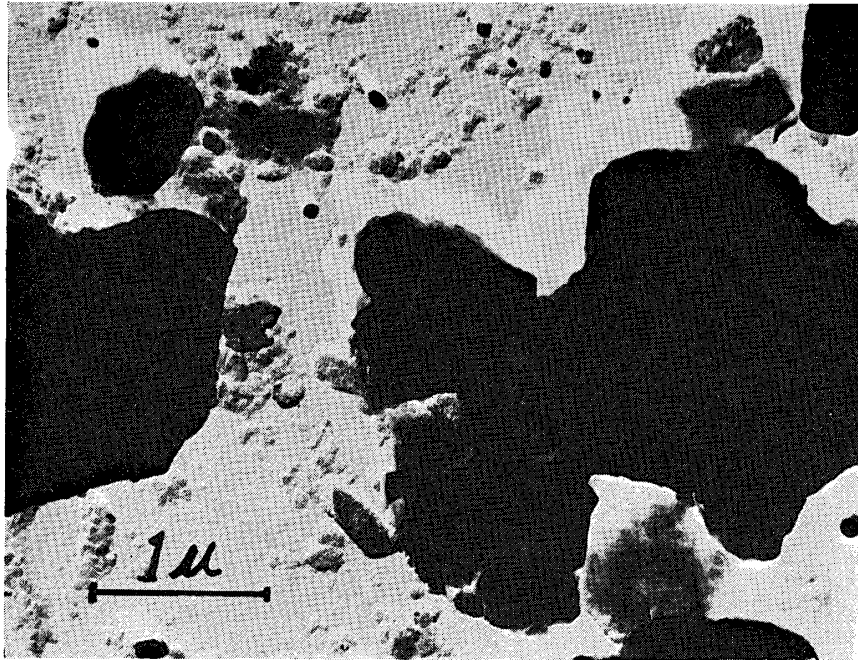


Fig. 3-B. Electron-micrographs of B-12 (upper) and C-12 (lower) after NaOH-treatment.



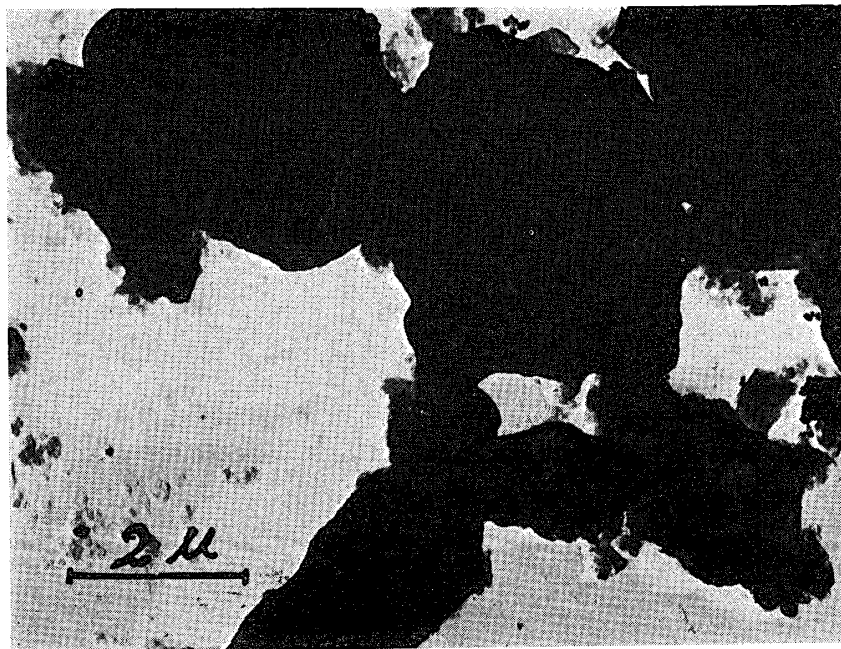
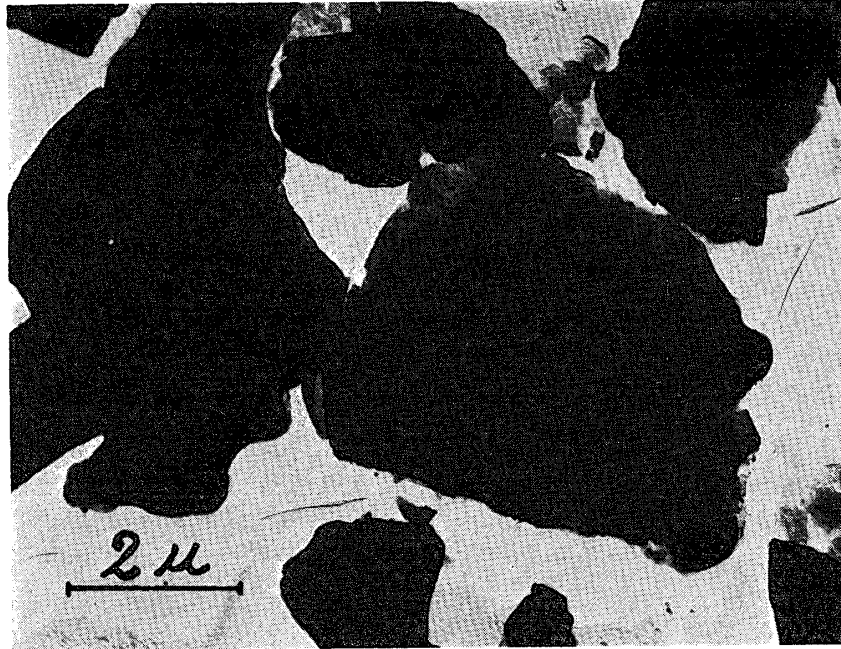


Fig. 3-C. Electron-micrographs of B-13 (upper) and C-13 (lower) after NaOH-treatment.

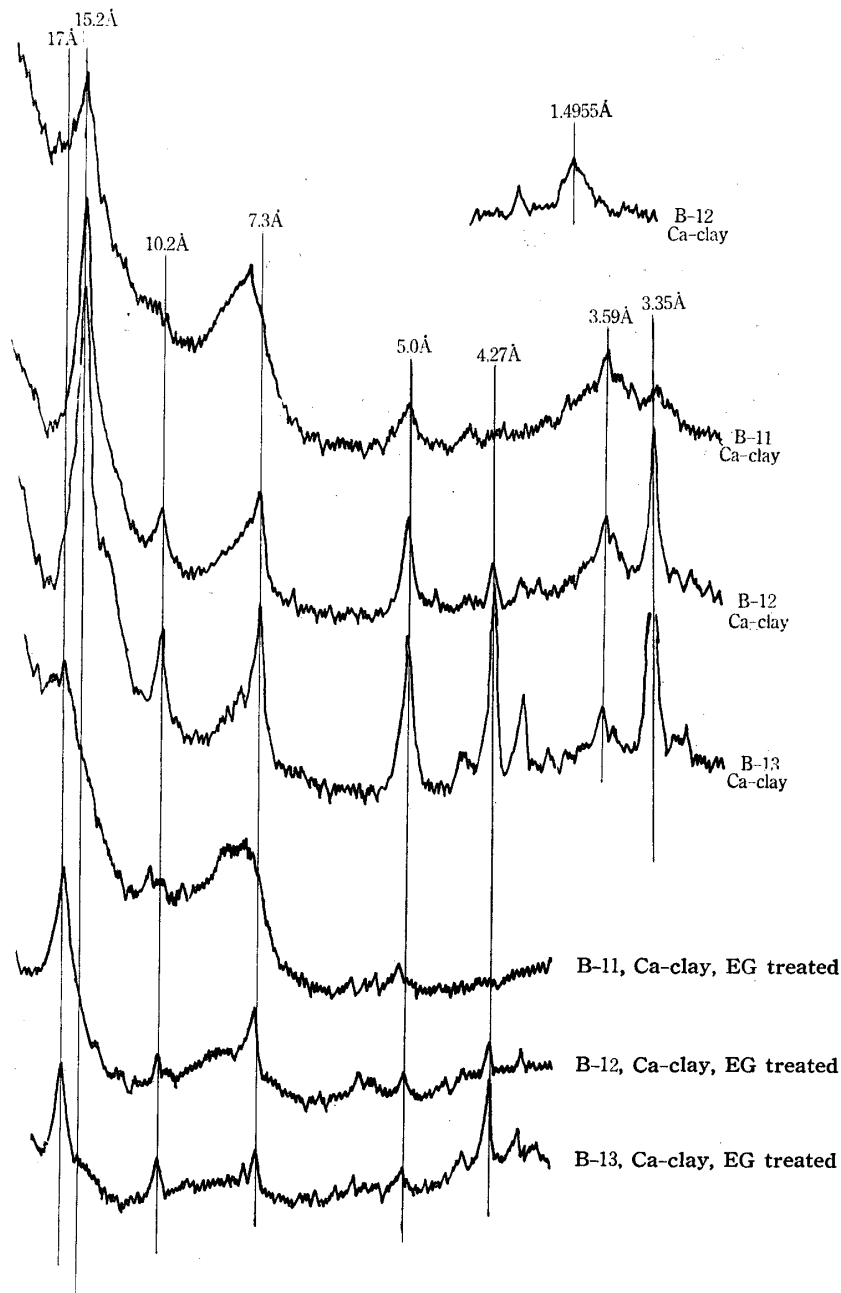


Fig. 4. X-ray diffraction patterns of Ca-clays and ethylene glycol solvated clays of B-11, B-12, and B-13.

After the ethylene glycol treatment of these Ca-clays, the 15.2 Å peaks expanded to 17 Å. When random specimens were used, 1.50 Å peaks occurred in all the samples. Therefore, the 15.2 Å peaks were identified to be the (001) diffraction of dioctahedral 2:1 expansible minerals.

The 10.2 Å peaks were stable to the heat treatment and did not expand with ethylene glycol solvation. Thus these peaks should be (001) diffractions of illitic minerals. The 7.3 Å peaks are (001) diffraction of halloysite as already clarified.

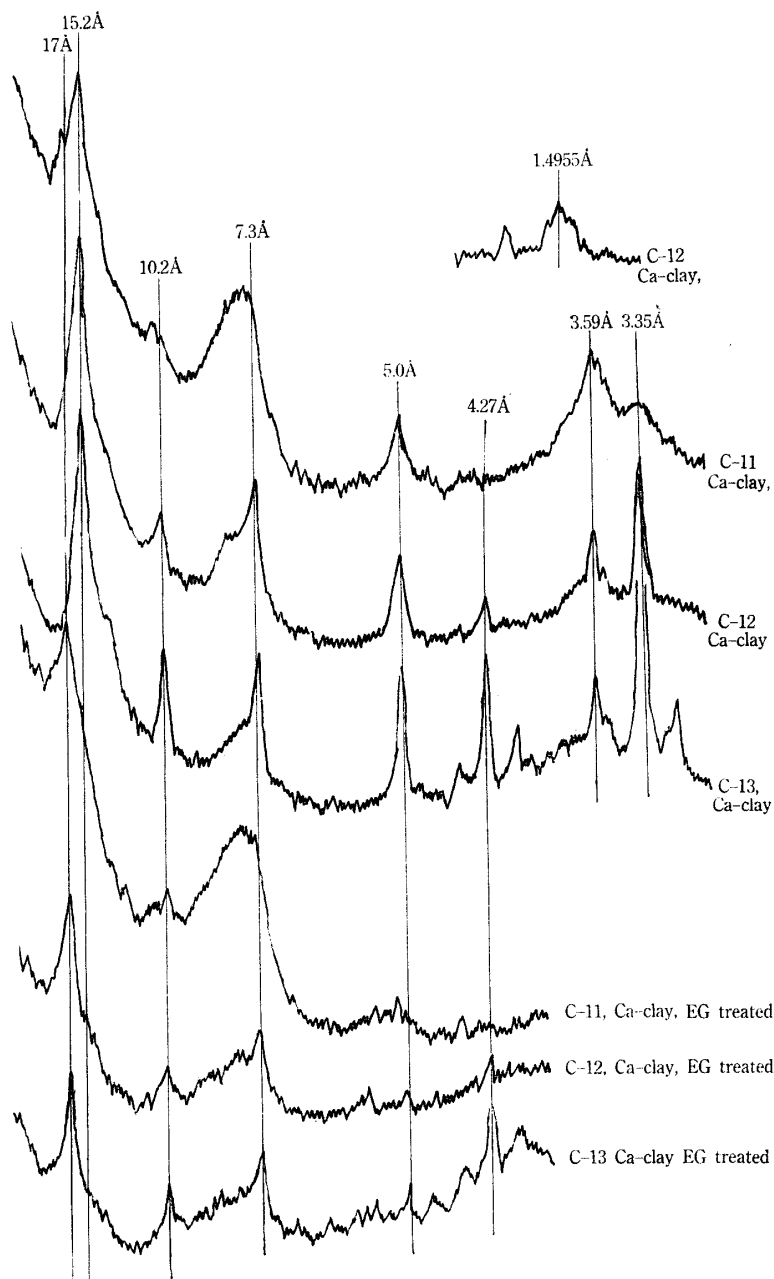


Fig. 5. X-ray diffraction patterns of Ca-clays and ethylene glycol solvated clays of C-11, C-12, and C-13.

The X-ray diffraction patterns of K-clays of C-11, C-12 and C-13 are given in Fig. 6. In case of C-11, when its K-clay was air-dried, the 15.2 Å peak shifted to 10.2 Å and broadened as seen in C-11-a. The ethylene glycol solvation of the clay resulted in the expansion of 10.2 Å to 12.4 Å (C-11-b). The spacing of expansion is presumed to be almost equivalent to the monolayer of ethylene glycol in the interlayers of 2:1 expansible minerals (13). This fact indicates that the 2:1 expansible mineral is different from montmorillonites. When K-clay

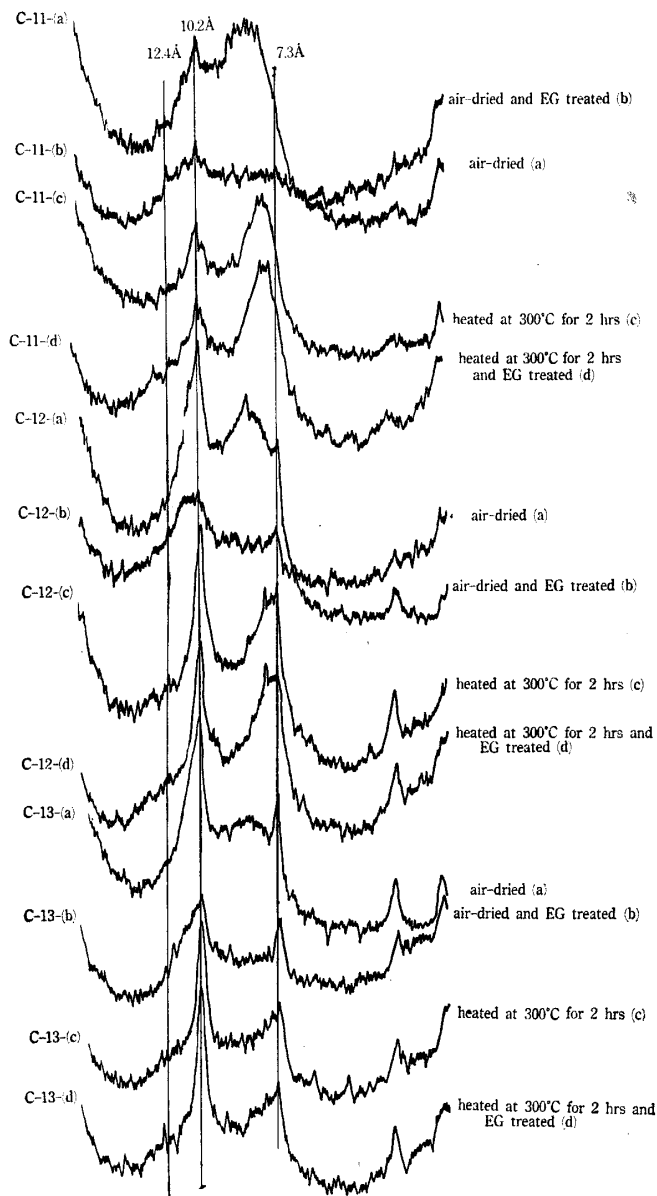


Fig. 6. X-ray diffraction patterns of K-clays of C-11, C-12, and C-13.

was heated at 300°C for 2 hrs., the 15.2 Å peaks collapsed to 10.2 Å (C-11-c) and did not expand by the ethylene glycol treatment (C-11-d).

Though almost the same results were obtained with C-12, medium size fraction, as with C-11, some differences were noted. The C-12 clay showed more intense and sharper 10.2 Å (C-12-a) than C-11 when air-dried and hardly expanded by the ethylene glycol treatment (C-12-b).

The peak intensity tends to increase with increasing of the size of the fractions. In case of C-13, the 10.2 Å peak of air-dried K-clay did not expand by the ethylene glycol solvation (C-13-b). These results may suggest that the properties of the 2:1 expansible minerals contained in each fraction became more

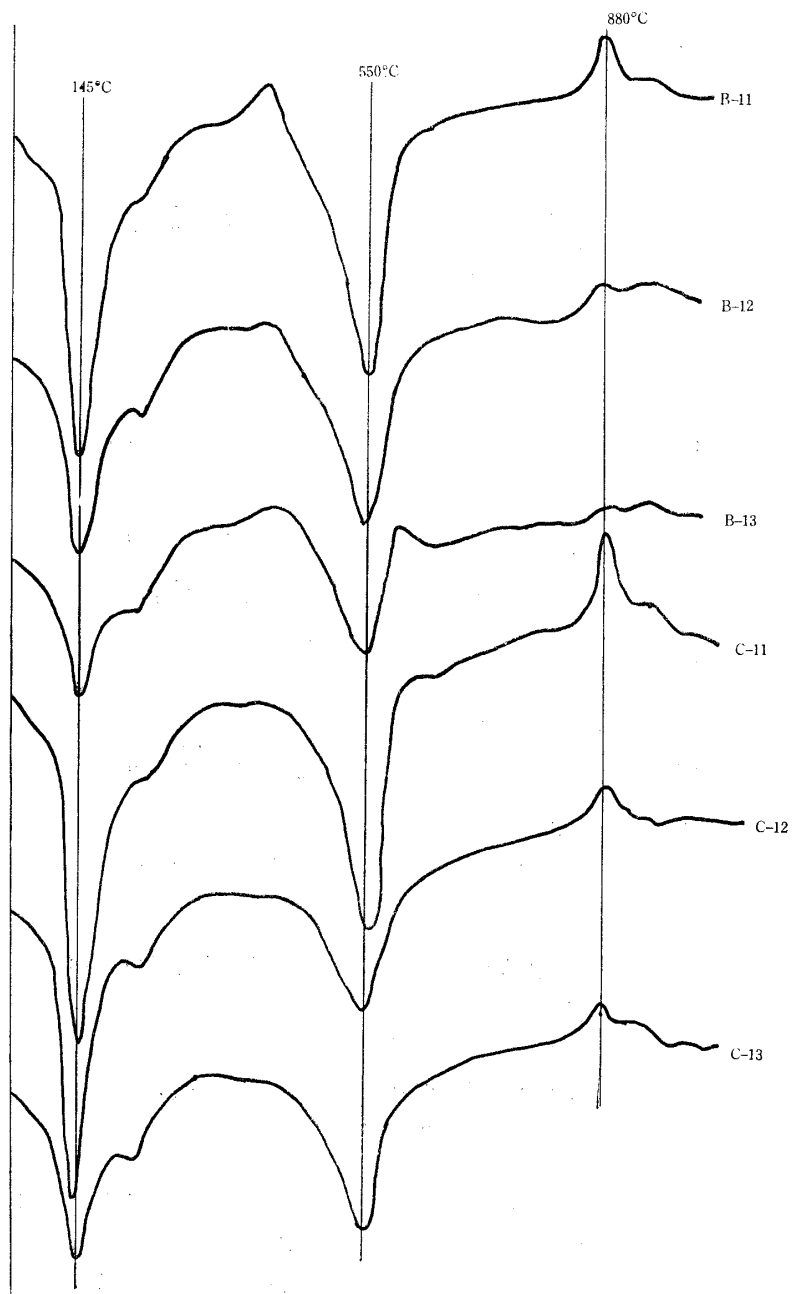


Fig. 7. Differential thermal curves of Ca-clays of size-fractionated B and C samples.

similar to those of vermiculite with the increasing of the clay size (13).

The differential thermal curves of Ca-clays of B-11, B-12, B-13, C-11, C-12 and C-13 are given in Fig. 7. Though the peak intensity was different with different size fractions, all the samples indicated almost the same peak temperatures of exothermic and endothermic reactions such as 145, 550 and 880°C.

The peak temperature of the second endothermic reaction, 550°C, is far lower than for hydrothermal montmorillonites. This fact has been observed with soil montmorillonites (14, 15, 16, 17).

The data of the total elemental analysis are shown in Table 3. The samples for the analysis were prepared as follows: The NaOH treatment without pre-heating was made on C-11 and C-12 and then clays equivalent to the size of 0.1 and 1.0  $\mu$  were collected by the centrifuge from C-11 and C-12, respectively. The exact sizes of these samples were determined by the electron micrographs. The mean sizes were 0.135  $\mu$  for C-11 (C-11f) and 0.97  $\mu$  for C-12 (C-12-f).

Table 3. Total elemental analysis of C clays which were NaOH-treated.

	C-11-f (mean size 0.135 $\mu$ )	C-12-f (mean size 0.97 $\mu$ )
SiO <sub>2</sub>	50.48(%)	62.35(%)
Al <sub>2</sub> O <sub>3</sub>	27.90	20.21
Fe <sub>2</sub> O <sub>3</sub>	5.55	4.03
(FeO)	(0.21)	(0.26)
TiO <sub>2</sub>	2.10	2.12
MnO	tr.	tr.
MgO	0.99	0.83
CaO	tr.	tr.
K <sub>2</sub> O	1.66	2.46
Na <sub>2</sub> O	0.16	0.50
+ H <sub>2</sub> O		
{ 110-250°C	1.20	0.42
{ 250-350°C	1.54	0.62
{ 350-600°C	7.56	5.65
{ 600-800°C	0.85	0.79
Total	100.26	99.98
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	3.07	5.24
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub>	2.72	4.65

There are found several facts which are common to C-11-f and C-12-f. The low contents of Fe<sub>2</sub>O<sub>3</sub>, MnO and MgO characterize the clays. These elements are presumed to be present in the octahedral layers of 2:1 minerals. The existence of relatively high amounts of TiO<sub>2</sub> and water should be noted.

On the contrary, differences between C-11-f and C-12-f are pointed out in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O contents. C-11-f has lower SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, than C-12-f, which contains some amounts of quartz as seen in the X-ray diffraction patterns.

More K<sub>2</sub>O was determined in C-12-f than in C-11-f. The high crystallinity of the coarser clay fraction is presumed to be associated with the more stable potassium fitting in the interlayers of 2:1 minerals. This presumption is supported

by the potassium fixation.

CEC, glycerol absorption and potassium fixation are showed in Table 4. Higher CEC and glycerol absorption were obtained for C-11-f than for C-12-f. On the contrary, potassium fixation was smaller for C-11-f than C-12-f. The amounts of fixed potassium were equivalent to 31 per cent of CEC for C-11-f and 45 per cent of CEC for C-12-f.

**Table 4.** CEC, cation exchange capacity, glycerol absorption and potassium fixation of C-11-f and C-12-f.

	C-11-f	C-12-f
CEC (me/100g)	53.3	43.6
Glycerol absorption (%)	14.54	10.98
K <sub>2</sub> O fixed (%)	0.783	0.934
(me/100g)	16.6	19.8

On the basis of the above data, the minerals contained in C-11-f and C-12-f were approximately computed as indicated in Table 5 (18). Excluding the quartz, the contents of 1:1 minerals was higher in C-11-f than C-12-f. Almost the same amounts of 2:1 expansible minerals were seen in both samples. The amounts of illitic minerals were higher in C-12-f than in C-11-f. This may be associated with the crystallinity of the coarser clay fractions as mentioned before.

**Table 5.** Calculated amounts of crystalline minerals in C-11-f and C-12-f (% in 110°C dry basis).

Minerals	C-11-f	C-12-f
1:1 mineral (halloysite)	16-20	5-10
2:1 expansible minerals	63-67	51-55
Illitic minerals	17	25
Quartz	0	10-15

On the other hand, the amounts of minerals contained in C-O (<2 $\mu$  fraction, only NaOH-treated) were approximately calculated as follows; 2:1 expansible minerals, 50~60 per cent, illitic minerals, 20 per cent, 1:1 minerals, 10~20 per cent, and quartz, 5~10 per cent. These minerals are presumed to exist in B-O as in C-O.

### Summary

The identification of crystalline clay minerals were conducted on the clay fractions of B and C horizons of a diluvial soil. The 2:1 expansible clay minerals were found in major amounts. Illitic minerals, 1:1 clay minerals and quartz were

also present in small amounts.

The crystals of 2:1 expansible clay minerals were platy and irregular in shape and clear in the hems. Thus the minerals seem to be similar to illites in morphology.

The low contents of Mg, Fe (II) and Mn characterized the 2:1 minerals. So the considerable amounts of negative charges of the clay were presumed to be due to the substitution of Al for Si in the tetrahedral layers.

Especially the coarser 2:1 expansible clay minerals easily collapsed to 10.2Å when they were K-saturated and air-dried, and did not expand by the ethylene glycol solvation. Also the minerals had some amounts of fixed potassium. According to these properties, it can be said that the 2:1 expansible minerals are vermiculite-like.

It was noticeable that large amounts of water existed at temperatures higher than 250°C. Also the second endothermic reaction of the minerals appeared at 550°C in DTA.

### Acknowledge

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