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Mineralogical and Agrochemical Properties of Kawatabi Volcanic Ash Soil.

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Summary

The profile of Kawatabi volcanic ash soil consists of present-day and buried soils underlaying dacitic tuff. The studies of primary minerals and chemical composition of ferromagnetic minerals indicated the presence of at least two kinds of felsic volcanic ash from which the present-day and buried soils were derived. According to the results of carbon dating, the former is older than 1000 years, but younger than 3200 years. The latter soil is older than 4500 years.

The essential clay minerals of all the soil samples were Al-interlayered 2:1 layer silicates accompanying small amounts of illite, kaolinite, chlorite, opaline silica, quartz and cristobalite. However, the existence of allophane in the soil was not confirmed.

The A-horizons of both present-day and buried soils were extremely rich in humus. High phosphate absorption by the soil samples was found throughout the profile. Reflecting the felsic property of the parent materials, the pH values, the degrees of base saturaton and the total and available copper and zinc of all the samples were very low.

The visible zinc deficiency of dent corn was found by the greenhouse experiments using the present-day and buried soils. On the other hand, the hidden copper deficiency of the same plant was ascertained by leaf analysis.

TABLE 1. *Some Properties*

Sample No	Depth (cm)	Soil color	Soil texture	pH (H_2O)	Total C (%)	Total N (%)	C/N	CEC (me/100 g)
1	0-12	7.5YR2/1	LiC	4.40	14.01	0.85	16.48	27.17
2	12-15	7.5YR2/2	L	5.00	6.42	0.38	18.88	15.67
3	15-26	5YR2/1	CL	5.10	13.35	0.51	26.18	26.43
4	26-40	5YR1.7/1	SL	5.10	13.60	0.84	16.19	25.00
5	40-54	10YR2.5/2	SL	5.20	9.90	0.78	12.69	24.11
6	54-81	10YR4/6	LS	5.45	2.76	0.17	16.24	12.05
7	81-	10YR5/6	LS	5.50	1.31	0.09	14.56	10.54

In 1960, Uchiyama, Masui and Onikura (1, 2) reported that the clay fraction of the Kawatabi volcanic ash soil was composed mainly of an expansible 2:1 layer silicate. They emphasized that volcanic ash soil in which clay fraction predominates by an expansible 2:1 layer silicate, as in the soil of the Kawatabi district, had been found nowhere else in Japan and its formation was related to the felsic property of the parent materials. Since then a considerable number of volcanic ash soils in which clay fraction predominate by 2:1 layer silicates have been found in Northern Japan (3–5).

The purpose of the present investigation is not only to ascertain that in the clay fraction of Kawatabi soil a 2:1 layer silicates predominates, as Uchiyama et al (1, 2) reported, but also to determine some agrochemical properties of the soil.

Materials and Methods

The soil samples used in this study were collected at the top of a hilly region in Katsurashimizu, Rokkaku area, Kawatabi district. The description of climate, topography, vegetation and so on of this area has already been given by Uchiyama et al (1.2).

A brief description of the soil profile and some analytical data of the soil are shown in Table 1. Though the soil has two humus horizons, the number of parent materials is considered to be at least three kinds. The first (0–15 cm in depth) and second ones (15–54 cm) are volcanic ash and the third one is weathered dacitic tuff.

According to results of carbon-dating of humic acids obtained by Yamane,* the first layer is 990±80 years old and the third layer is 3190±95 years old. Therefore, the age of present-day soil (0–15 cm) is older than 1000 years, but younger than 3200 years. The buried soil (15–54 cm) is older than 4500 years.

of the Soil Samples

Exchangeable bases (me/100 g)				Degree of base saturation (%)	Phosphate absorption (mg P_2O_5/100 g)	Carbon dating[1)] (years, Bp)
Ca	Mg	K	Na			
0.59	0.42	0.69	0.18	6.9	2091	990±80
0.22	0.09	0.34	0.17	5.2	2002	
0.27	0.02	0.36	0.14	3.0	2671	3190±95
0.29	0.04	0.19	0.15	2.7	2730	
0.21	0.02	0.15	0.12	2.1	2797	4450±100
0.09	0.02	0.14	0.11	3.0	2296	
0.05	0.03	0.13	0.08	2.8	1735	

1) Measured by I. Yamane (1973)

* Yamane, I., Personal communication (1973)

For the microscopic analysis of parent materials, the 0.1 to 0.2 mm sand fraction was separated into heavy and light minerals with bromoform (2.9 in specific gravity). The mineral composition of the fraction was determined under the microscope in the usual way. The chemical composition of ferromagnetic minerals was determined by the methed of Shoji et al (6). The whole clay fraction ($<2\mu$) was separated from the soil samples by the sedimentation method, after 6 per cent hydrogen peroxide treatment, and submitted to the analysis of X-ray diffraction, infrared absorption spectroscopy, and electron micrography.

The fine clay fraction ($<0.2\mu$) was also used for some experiments after separating by the centrifugation of the deferrated clay specimen (7).

X-ray diffraction patterns of orientated specimens were obtained with Cu-Kα radiation (45 KV, 30 mA) using Rigaku Denki, Geigerflex. Infrared absorption spectra were measured by using a Hitachi infrared spectrometer Model EPI-S_2. Electron micrographs were taken by JEOL Model JEM 100B with a direct magnification of 3,000 to 10,000 $\times$.

Total copper and zinc of the soil samples were analysed by an atomic absorption spectrometer after the samples were digested using a mixed solution of concentrated HNO_3, $HClO_4$ and HF solutions. Available soil copper and zinc extracted using a 1N HCl solution were also analysed by an atomic absorption spectrometer (8).

Both virgin surface (0–12 cm) and buried (15–40) soils were used for the greenhouse experiment for available soil copper and zinc. Nutrients such as NH_4 Cl (0.69 g per pot), KH_2PO_4 (1.90 to 2.59 g per pot), $MgSO_4 \cdot 7H_2O$ (1.65 g per pot) and certain amounts of micronutrients (8 ppm of Mn, 5 ppm of Cu and Zn, 3 ppm of Mo and 0.5 ppm of B) were applied to each plastic pot containing 450 g of dry soil after liming to adjust the soil pH to 6.0, 6.5 and 7.0. Two seedlings of dent corn per pot were transplanted and were taken for analysis after 16 days of growing in the greenhouse.

Results and Discussion

1. *Some Chemical Properties of Soil Samples*

As seen in Table 1, the humus contents in the first, third and forth layers are very high, as in the surface horizons of many volcanic ash soils. Both pH values and degree of base saturation of all the layers of the soil are extremely low, presumably reflecting the felsic property of the parent materials. High phosphate absorption, which is characteristic of the volcanic ash soils, is also observed for these soil samples.

2. *Primary Mineral Composition of Soil Samples*

According to Table 2, the minerals in the sand fractions of all the samples are volcanic glasses of vesicular and transparent types, plagioclase, hypersthene, ferromagnetic minerals, augite, hornblende and quartz. However, the amount of each mineral changes considerably from the surface to subsoil. Based on the mineral composition, it is concluded that the parent materials of these soils are dacitic.

The sixth layer seems to be transitional from volcanic ash to weathered dacitic tuff, and the layers below it are weathered dacitic tuff. The differences in the degree of weathering of augite crystals are observed between the present-day and buried soils. Augite crystals are considerably fresh in the former.

TABLE 2. *Primary Mineral Composition of Sand Fractions (0.1–0.2 mm)*

Sample	% of Heavy minerals	Heavy mineral (%)					Light mineral (%)				Degree of weathering[1] (%)		
									Vol. glass				
No		Hy.	Au.	Hb.	Mt.	Un.	Pl.	Qz.	Ves.	Trans.	1	2	3
1	8	56	14	5	21	4	30	tr	29	41	41	31	28
2	3	56	19	5	20	tr	10	tr	32	58	66	21	13
3	9	55	10	4	28	3	33	1	22	44	11	39	50
4	9	50	11	8	27	4	44	1	23	32	23	44	33
5	6	47	15	12	24	2	38	1	33	28	33	33	34
6	8	43	9	19	25	4	40	1	38	21	18	48	34
7	11	49	8	11	30	2	33	1	55	11	33	48	19

Hy, hypersthene; Au, augite; Hb, hornblende; Mt. ferromagnetic mineral; Un, unknown; Pl, plagioclase; Qz, quartz; Ves, vesicular type; Trans, transparent type,
1) Degree of etching of augite, 1, low; 2, medium; 3, high

3. *Chemical Composition of Ferromagnetic Minerals*

Shoji et al. (6) reported that the chemical composition of ferromagnetic minerals separated from volcanic ashes was highly useful for the identification of volcanic ash layers or their origins. The analytical data of Table 3 indicates that the contents of various elements except titanium are almost the same. This fact suggests that the parent materials of these soils were derived from the same volcano, presumably Narugo volcano (2). However, the difference in titanium content

TABLE 3. *Chemical Composition of Ferromagnetic Minerals*

Sample No	T-Fe %	TiO_2 %	V_2O_3 ppm	MnO ppm	ZnO ppm	V/T-Fe $\times 10^{-4}$	Zn/Ti $\times 10^{-4}$
1	60.15	11.38	2.672	6.564	1.128	30.21	132.8
2	58.68	12.57	2.653	7.545	1.107	30.74	118.0
3	61.97	9.38	2.590	6.499	1.154	28.42	164.9
4	61.99	9.21	2.680	7.217	1.154	29.40	167.9
5	62.23	9.13	2.787	6.660	1.132	30.45	166.1
6	61.01	8.84	2.534	6.778	1.135	28.24	172.1
7	62.45	9.11	2.683	6.431	1.119	29.21	176.4

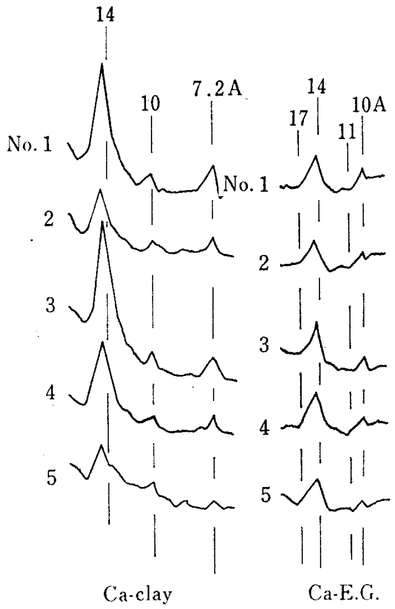

FIG. 1. X-ray Diffraction Patterns of the Clay Specimens.

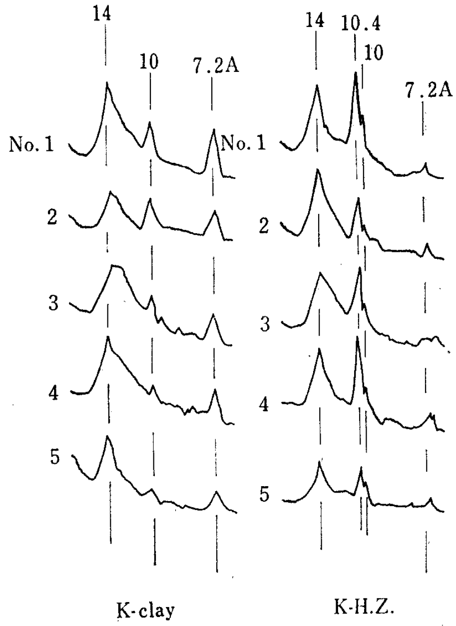

FIG. 2. X-ray Diffraction Patterns of the Clay Specimens.

between the two soils is considered to be due to different eruptions of the volcano.

4. *Clay Mineral Composition of Soil Samples.*

Clay mineral compositions of the volcanic ash soil layers were studied using X-ray diffraction patterns, infrared absorption spectra and electron micrographs.

1) X-ray analysis

X-ray diffraction patterns obtained from the orientated specimens are shown in Figs. 1, 2 and 3. All the clay specimens ($<2\mu$) saturated with Ca^{2+} ions show the intense 14 Å peaks and small 10 Å and 7 Å peaks (Fig. 1). Both 14 Å and 10 Å peaks hardly expand after the treatment with ethylene glycole. Therefore, the latter peak is the (001) diffraction of illite.

The 7 Å peaks (exactly 7.1 to 7.2 Å) of all the specimens largely shift to 10.4 Å after the hydrazine treatment of K-saturated clay specimens, indicating that almost all of 7 Å peaks are (001) of kaolinite and (002) of neglegebly small amount of chlorite.

Comparing the results of the present investigation with those of the previous papers (1, 2), it should be noted that there is a difference in the expansibility of 2:1 layer silicates which are the main crystaline clay minerals of the Kawatabi soil. This difference is considered to be caused by the difference in the pretreatment of the clay specimens. The senior authors (1, 2) used relatively drastic deferration treatment which might remove the interlayered hydroxyl aluminium from the 2 : 1 layer silicates. On the contrary, in this investigation any pretreatment except the

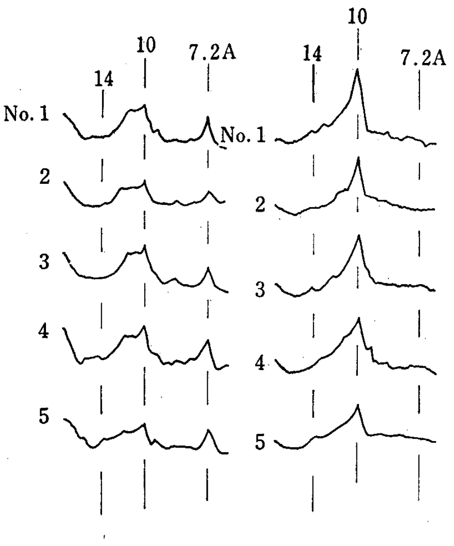

Fig. 3. X-ray Diffraction Patterns of the Clay Specimens.

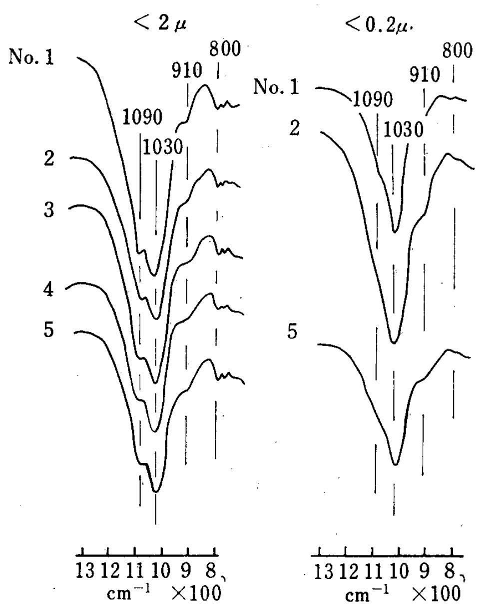

Fig. 4. Infrared Absorption Spectra of the Clay Specimens.

hydrogen peroxide treatment was not conducted for preparing the clay specimens for X-ray analysis.

2) Infrared absorption spectroscopy

Infrared absorption spectra of Mg-saturated clay less than 2 and $0.2\,\mu$ were obtained through the wave numbers ranging from 4000 to 640 cm^{-1}. About 0.3 mg of the clay specimens were mixed with 170 mg of KBr.

As shown in Fig. 4, the infrared absorption spectra of the whole clay fraction ($<2\,\mu$) occur at about 1090, 1030, 910 and 800 cm^{-1} in all the specimens. Since all the clay specimens contain quartz and cristobalite, the absorption bands at 1090 and 800 cm^{-1} are due to these minerals. The doublet at 800 cm^{-1} clearly indicates the existence of quartz. The absorption at 1030 and 910 cm^{-1} are attributable to 2:1 layer silicates. Since the fine clay specimens ($<0.2\,\mu$) do not contain these silica minerals, they show only the bands at 1030 and 910 cm^{-1} arising from 2:1 layer silicates. It is interesting that any broad absorption between about 1000 and 900 cm^{-1} indicating the presence of allophane is not observed.

3) Electron Micrography

The electron micrographs of Na-saturated clay less than 2 and $0.2\,\mu$ are shown in Plate 1. In the electron micrographs of the whole clay fractions, there can be observed three kinds of particles; platy particles of 2:1 layer silicates, circular and elliptical particles of opaline silica, and electron dense particles which are considered to be volcanic glass, quartz and so on. The particles of opaline silica are relatively abundant in the humus layer of the present-day soil as previously reported (9). These particles in the humus layers of buried soil are small in number and are strongly weathered. In the case of electron micrographs of the fine clay fractions, only plate-like particles of 2:1 layer silicates are present. As expected from the infrared spectra, allophane particles like grape tufts or extremely small spheres are rarely seen.

Summarizing the clay mineralogical studies mentioned above, it is concluded that the main clay minerals in the Kawatabi volcanic ash soil are Al-interlayered 2:1 layer silicates accompanied by small amounts of illite, kaolinite, chlorite, opaline silica, quartz and cristobalite. However, the existence of allophane in the soil was not evident.

5. *Copper and Zinc Status*

1) Total and available soil copper and zinc

The amounts of total copper and zinc in the present-day soil samples are much smaller than those of the buried soil samples as shown in Table 4. On the contrary, the contents of available copper and zinc are in contrast with those of total copper and zinc. However, compared with the total and available amounts of both elements in volcanic ash soils derived from intermediate or mafic parent materials (8), those of the Kawatabi soil show considerably low values, reflecting the felsic property of the parent materials.

TABLE 4. *The Contents of Total and Available Copper and Zinc in the Soil Samples*

Sample No	Copper (ppm)		Zinc (ppm)	
	Total	Available[1]	Total	Available[1]
1	10.2	1.7	29.4	6.9
2	7.1	1.4	23.1	2.2
3	15.9	0.8	54.7	1.3
4	15.4	0.8	52.9	1.3
5	13.1	0.7	63.1	1.2
6	13.4	0.7	85.5	2.6
7	15.8	0.9	85.7	3.0

1) Extracted by 1N HCl solution

2) Greenhouse experiment of dent corn.

As seen in Table 5, the seedlings of dent corn grew much better at both pH 6.5 and 7.0 plots than at pH 6.0 plots. However, the plants grown on the plots without a micronutrient supply are much inferior to those on the plots with full nutrient supply. This fact suggests that the seedlings of dent corn suffer from a deficiency of copper and zinc. The typical symptoms of zinc deficiency such as rosseting, chlorosis and accumulation of antocyanin were observed in the buried soil plots. Though no visible symptom of copper deficiency was found, a leaf

TABLE 5. *The Growth of Dent Corn Seedlings Grown with or without Micronutrient Supply*

Soil	Treat-ment	pH 6.0 Height (cm)	pH 6.0 D.W. of shoot(g)	pH 6.5 Height (cm)	pH 6.5 D.W. of shoot(g)	pH 7.0 Height (cm)	pH 7.0 D.W. of shoot(g)
Present-day soil	FN	52.4	0.69	61.4	0.86	59.5	0.97
	-All			47.5	0.76		
	-Zn	47.4	0.70	54.0	0.76	59.8	0.88
	-Cu	54.3	0.72	60.4	0.97	54.0	0.79
Buried soil	FN	46.8	0.62	55.3	0.82	52.8	0.81
	-All	32.4	0.40	47.5	0.72	41.6	0.65
	-Zn	38.6	0.45	44.6	0.74	36.0	0.53
	-Cu	46.3	0.54	54.6	0.92	47.6	0.74

D.W., Dry weight; FN, with full nutrient supply; -All, without all micronutrient supply; -Zn, without zinc supply; -Cu, without copper supply

analysis showed that the copper contents of the plants grown on the plots without copper supply were near the critical value (1.96 to 3.64 ppm of Cu).

Using the same volcanic ash soil for the greenhouse experiments, Tsutsumi *et al* (10–12) found copper and boron deficiencies in barley, lucerne, orchard grass and lettuce.

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References

1) Uchiyama, N., Masui, J., and Onikura, Y., *Trans. 7th Intern. Cong. Soil Sci*, **4**, 443 (1961)
2) Uchiyama, N., Masui, J., and Onikura, Y., *Soil Sci. and Plant Nutr.*, **8**, 13 (1962)
3) Uchiyama, N., Masui, J., and Shoji, S., *J. Sci. Soil Manure*, **39**, 110, 114 and 411 (1968)
4) Masui, J., Shoji, S., and Uchiyama, N., *Tohoku J. Agr. Res.*, **17**, 17 (1966)
5) Masui, J., and Shoji, S., *Proc. Intern. Clay Confer.* (Tokyo), **1**, 383 (1969)
6) Shoji, S., Kobayashi, S., and Masui, J., *J. Jap. Assoc. Min. Petr. Ec. Geol.* in press (1974)
7) Mehra, O.P., and Jackson, M.L., *Clays Clay Minerals* **5**, 317 (1960)
8) Minami, K., Shoji, S., and Masui, J., *Tohoku J. Agr. Res.*, **23**, 65 (1972)
9) Shoji, S., and Masui, J., *J. Soil Sci.* **22**, 101 (1972)
10) Tsutsumi, M., and Fujiwara, A., *Tohoku J. Agr. Res.*, **17**, 101 (1966)
11) Tsutsumi, M., Ohira, K., and Fujiwara, A., *J. Sci. Soil Manure*, **38** 459 (1967)
12) Tsutsumi, M., Ohira, K., and Fujiwara, A., *J. Sci. Soil Manure* **39** 121 (1968)

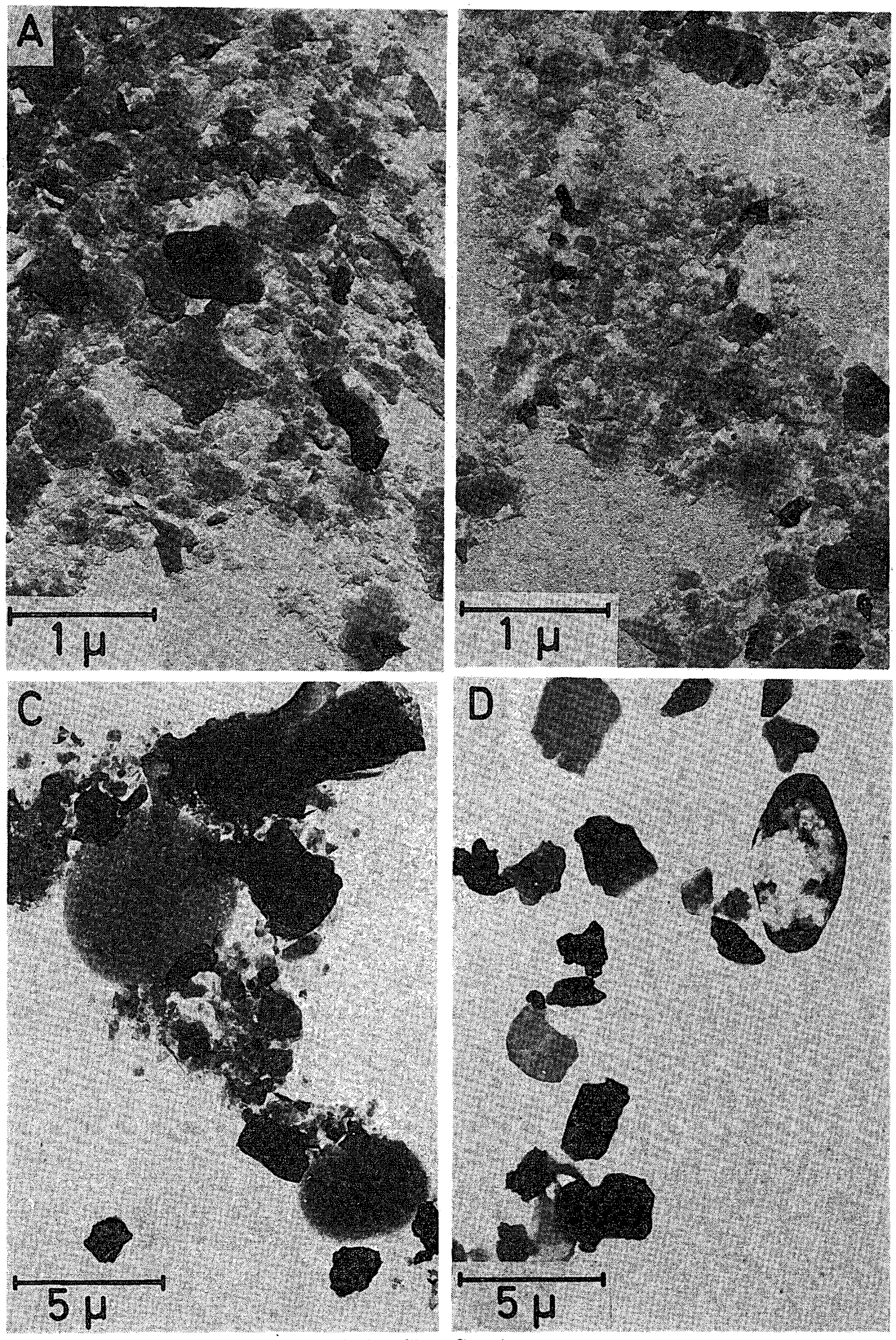

PLATE 1. Electron Micrographs of the Clay Specimens.

A: $<0.2\ \mu$ fraction of No. 1 sample B: $<0.2\ \mu$ fraction of No. 5 sample

C: $<2\ \mu$ fraction of No. 1 sample D: $<2\ \mu$ fraction of No. 3 sample