

Clay Minerals Of Some So-called Degraded Paddy Soils. Part 1 : Nature of clay fractions of the Nyuzen soil, Toyama Prefecture and the Yokita soil, Kagawa Prefecture

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CLAY MINERALS OF SOME SO-CALLED DEGRADED PADDY SOILS. PART 1

Nature of clay fractions of the Nyuzen soil, Toyama
Prefecture and the Yokita soil, Kagawa Prefecture

SHIGENORI AOMINE AND TOSHIO HIGASHI

In general, so-called degraded paddy soils are those having small quantities of iron and manganese in soil material from the A horizon which often is a bleached, white or grey layer. It is a common characteristic of the paddy soil having the low level of underground water, that iron and manganese are eluviated from the A horizon of the soil and deposited in the B horizon. The degraded paddy soil is usually sandy in texture, and is often observed in districts of granitic, siliceous sandstone, or gneissic soils. It is suggested that severe percolation and a small amount of iron and manganese in the parent material are the greatest causes of the degraded paddy soil, and ultimately affect the clay fraction. However, the mineralogical composition of the clay fraction in the degraded paddy soil has received little attention. The purpose of this work is to investigate the mineralogical nature of the clay fractions of some typical so-called degraded paddy soils.

In this study, identification of clay minerals was made by comparing several properties of the clay fractions with those of clay minerals in the reference books (2, 4), as experience has shown that identification of the clay mineral of soils was most reliable when they are based on measurements of several properties. The properties used for the comparison were: differential thermal and dehydration curves, chemical composition, ethylene glycol retention, cation-exchange capacity, electron micrograph, and x-ray diffraction pattern.

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MATERIALS AND METHODS

Soil samples used in this work were taken from two typical degraded paddy fields in Toyama and Kagawa prefectures. Their profile characteristics are given in Table 1.

Table 1. Soil samples used.

| Sample number | Horizon | Depth | Characteristics |
|--|----------------|----------|--|
| Locality: Nyuzen-machi, Shimoshinkawa-gun, Toyama Prefecture | | | |
| 361 | A | 0-18 cm. | Friable dark grey loam |
| 362 | B ₁ | 18-34 | Light grey sandy loam, with little yellowish brown streaks |
| 363 | B ₂ | 34-49 | Light grey sandy loam, with little blackish brown streaks |
| 364 | G ₁ | 49-62 | Light grey sandy loam, with little dark brown mottlings |
| 365 | G ₂ | 62-72 | Grey sandy loam, with little yellowish brown mottlings |
| Locality: Yokita-mura, Nakatado-gun, Kagawa Prefecture | | | |
| 403 | A ₁ | 0-13 | Friable grey loam |
| 404 | A ₂ | 13-18 | Light grey loam |
| 405 | B ₁ | 18-23 | Yellowish loam, with much brownish mottlings |
| 406 | B ₂ | 23-38 | Dark grey loam, with little brownish mottlings |

The air-dried samples were sieved to remove gravel, and fine earths (<2 mm. materials) were used for chemical, mineralogical, and physical analyses and for preparation of clay fractions. Some physical and chemical properties examined are shown in Table 2, and chemical composition of the fine earths is given in Table 3. These results reveal no properties peculiar to the paddy soils, although the silica content is somewhat high in all horizons and the amount of iron and manganese is low in the soils—especially surface soils as compared to common paddy soils. Cation-exchange capacity is rather low, too.

Mineralogical composition of the fine sands of the soil samples is shown in Table 4. The amount of heavy minerals (sp. gr. >2.70)

Table 2. Physical and chemical analyses of the fine earths.

| | | Nyuzen soil | | | | | Yokita soil | | | |
|--------------------------------|-------------------|-------------|------|------|------|------|-------------|------|------|------|
| | | 361 | 362 | 363 | 364 | 365 | 403 | 404 | 405 | 406 |
| Coarse sand (2-0.2 mm.) | (%) | 11.7 | 13.5 | 15.0 | 17.2 | 18.3 | 13.3 | 13.5 | 17.5 | 19.9 |
| Fine sand (0.2-0.02 mm.) | (%) | 37.3 | 44.7 | 38.5 | 41.5 | 54.9 | 30.7 | 27.5 | 27.7 | 27.6 |
| Silt (0.02-0.002 mm.) | (%) | 40.8 | 26.8 | 39.8 | 34.5 | 19.6 | 37.8 | 36.4 | 36.6 | 29.1 |
| Clay (<0.002 mm.) | (%) | 10.2 | 15.0 | 6.7 | 6.8 | 7.2 | 18.2 | 22.6 | 18.2 | 23.4 |
| pH(H ₂ O) | | 5.2 | 5.7 | 5.9 | 6.2 | 5.9 | 6.2 | 6.4 | 6.3 | 6.7 |
| Exchange acidity | (y ₁) | 2.2 | 2.3 | 0.2 | 0.6 | 0.6 | 1.0 | 0.8 | 3.1 | 0.6 |
| Hydrolytic acidity | (y ₁) | 9.4 | 3.8 | 5.6 | 3.3 | 3.6 | 6.0 | 5.6 | 3.3 | 3.4 |
| Total organic carbon (C) | (%) | 1.07 | 0.40 | 0.26 | 0.19 | 0.20 | 2.10 | 0.46 | 0.47 | 0.48 |
| Total nitrogen (N) | (%) | 0.13 | 0.05 | 0.03 | 0.03 | 0.03 | 0.29 | 0.09 | 0.09 | 0.07 |
| C/N | | 8.2 | 8.0 | 8.7 | 6.3 | 6.7 | 7.2 | 5.1 | 5.2 | 6.9 |
| Effect of air-drying (p.p.m.)* | | 78 | 57 | 28 | 9 | 4 | 29 | 31 | 22 | 11 |
| | (%) | 6.0 | 11.4 | 9.3 | 3.0 | 1.3 | 1.0 | 3.4 | 2.4 | 1.6 |
| C. E. C. § | (m.e./100 gm.) | 5.9 | 3.4 | 2.9 | 2.4 | 2.4 | 11.9 | 11.3 | 7.8 | 11.0 |
| Exchangeable Ca | (m.e./100 gm.) | 1.4 | 1.3 | 1.1 | 0.9 | 0.7 | 9.0 | 9.5 | 6.1 | 9.4 |
| Mg | (m.e./100 gm.) | 0.7 | 0.2 | 0.5 | 0.1 | 0.2 | 0.9 | 0.9 | 0.4 | 1.1 |

* Accumulation of ammoniacal nitrogen after incubation for 28 days in waterlogged condition at 28°C.

§ Cation-exchange capacity.

Table 3. Chemical composition of the fine earths.

| | | Nyuzen soil | | | | | Yokita soil | | | |
|--------------------------------|-----|-------------|--------|-------|-------|--------|-------------|-------|-------|--------|
| | | 361 | 362 | 363 | 364 | 365 | 403 | 404 | 405 | 406 |
| SiO ₂ | (%) | 65.42 | 65.10 | 65.66 | 66.05 | 65.50 | 75.47 | 72.27 | 76.83 | 76.16 |
| Al ₂ O ₃ | (%) | 16.98 | 18.67 | 16.64 | 15.75 | 16.27 | 9.62 | 9.65 | 9.44 | 10.38 |
| Fe ₂ O ₃ | (%) | 4.23 | 5.97 | 4.11 | 5.65 | 7.20 | 1.94 | 6.95 | 3.06 | 4.53 |
| MnO | (%) | 0.04 | 0.05 | 0.11 | 0.10 | 0.08 | 0.01 | 0.05 | 0.01 | 0.06 |
| CaO | (%) | 2.45 | 2.46 | 2.24 | 2.82 | 2.35 | 0.82 | 0.70 | 0.62 | 0.84 |
| MgO | (%) | 1.69 | 1.65 | 1.97 | 2.21 | 2.03 | 0.96 | 0.24 | 0.38 | 0.74 |
| K ₂ O | (%) | 2.03 | 2.13 | 1.67 | 1.33 | 2.38 | 1.71 | 1.38 | 1.91 | 1.63 |
| Na ₂ O | (%) | 2.25 | 2.12 | 3.49 | 2.76 | 2.68 | 0.91 | 0.67 | 1.33 | 0.95 |
| TiO ₂ | (%) | 0.50 | 0.53 | 0.53 | 0.51 | 0.55 | 0.22 | 0.22 | 0.44 | 0.42 |
| P ₂ O ₅ | (%) | 0.18 | 0.10 | 0.16 | 0.12 | 0.15 | 0.07 | 0.36 | 0.09 | 0.07 |
| Ignition loss | (%) | 4.60 | 2.78 | 2.53 | 2.40 | 1.99 | 8.92 | 6.59 | 5.10 | 5.64 |
| Total | (%) | 100.38 | 101.56 | 99.11 | 99.70 | 101.18 | 100.65 | 99.10 | 99.21 | 101.42 |

is very small (less than 1.5 per cent by weight) in all horizons of the Yokita profile, but that is moderate in the Nyuzen profile. The fine sands all consist dominantly of quartz, orthoclase, and plagioclase. In addition, small amounts of pyroxene, amphibole, muscovite, chlorite, and flakes of weathered light brown mica were found in the Nyuzen samples, while a trace of amphibole, pyroxene, and weathered mica was recognized in the Yokita soil.

Table 4. Mineralogical composition of fine sand separates (0.2-0.02 mm.).

| | Nyuzen soil | | | | | Yokita soil | | | |
|-----------------------------------|-------------|------|------|------|------|-------------|------|------|------|
| | 361 | 362 | 363 | 364 | 365 | 403 | 404 | 405 | 406 |
| Heavy mineral (sp. gr. >2.70) (%) | 8.6 | 9.3 | 8.5 | 9.9 | 7.5 | 0.2 | 1.5 | 0.2 | 0.8 |
| Light mineral (sp. gr. <2.70) (%) | 91.4 | 90.7 | 91.5 | 90.1 | 92.5 | 99.8 | 98.5 | 99.8 | 99.2 |
| Magnetite | —* | — | — | — | — | — | — | — | — |
| Rhombic pyroxene | + | ± | ± | ± | ± | ± | ± | ± | ± |
| Monoclinic pyroxene | — | — | — | — | — | — | — | — | — |
| Monoclinic amphibole | + | ± | + | ± | ± | ± | ± | ± | ± |
| Muscovite | ± | ± | ± | ± | ± | ± | — | — | — |
| Weathered mica | + | + | + | + | + | ± | ± | ± | ± |
| Chlorite | ± | ± | ± | ± | ± | — | — | — | — |
| Zircon | — | — | — | — | ± | — | — | — | ± |
| Quartz | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ |
| Orthoclase | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ |
| Plagioclase | — | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ | ⦿ |
| Microcline | — | + | + | — | — | — | — | — | — |
| Glass | — | — | — | — | — | — | — | + | + |

* ⦿: Abundant (30-60%), ⦿: Common (10-30%), ⦿: Occasion (5-10%),
 +: Rare (1-5%), ±: Very rare (<1%), —: None.

The fine earths were repeatedly treated with H_2O_2 on a steam bath to remove organic matter, dispersed for several hours with a small amount of NaOH in a rotatory shaker, and allowed to stand overnight. These suspensions were kept below pH 8.4. Clay fractions ($<2\mu$, $<0.5\mu$, and $<0.1\mu$) were separated by siphoning off the top suspension. The procedure of separation was repeated several times, and the suspensions thus obtained were coagulated with NaCl. The clay was transferred into a centrifugal tube, and repeatedly washed with n-NaCl or n-Ca acetate solution. The Na- or Ca-clay obtained here was washed with

methanol until free from chloride or calcium ions. After being air-dried the clay fraction was lightly crushed with an agate pestle in an agate mortar, and stored in a desiccator keeping relative humidity 36.8 per cent at 25°C. with 50 per cent H_2SO_4 .

Analytical methods used in this work were the same ones as in the previous work (1).

X-RAY ANALYSIS

The x-ray powder diffraction pattern for the clay samples saturated with ethylene glycol, or heated for 30 minutes at 600°C. are shown in Tables 5 and 6. Diffraction patterns of the clays of the Nyuzen soil all closely resemble one another—this is also true in the Yokita soil.

Table 5. X-ray diffraction data of clay fractions ($<2\mu$) saturated with ethylene glycol.

| 361 d(Å) i§ | 361* d(Å) i§ | 362 d(Å) i§ | 363 d(Å) i§ | 364 d(Å) i§ | 365 d(Å) i§ |
|----------------|-----------------|----------------|----------------|----------------|----------------|
| 15.1 III | 14.2 III | 15.1 III | 15.1 III | 15.1 III | 15.1 III |
| 10.0 III | 10.2 IV | 10.0 III | 10.0 III | 10.0 III | 10.0 III |
| 7.16 IV | | 7.16 IV | 7.16 IV | 7.16 IV | 7.16 IV |
| 4.84 VI | | 4.84 VI | 4.84 VI | 4.84 VI | 4.84 VI |
| 4.49 II | 4.49 III | 4.49 III | 4.47 III | 4.47 III | 4.47 III |
| 4.06 IV | 4.26 VI | 4.06 IV | 4.06 IV | 4.06 IV | 4.06 IV |
| | | 4.05 VI | | | |
| 3.73 V | 3.73 V | 3.73 V | 3.73 V | 3.73 V | 3.73 V |
| 3.65 V | | 3.65 V | 3.65 V | 3.65 V | 3.65 V |
| 3.34 II | 3.35 III | 3.34 II | 3.34 II | 3.34 II | 3.34 II |
| 3.18 III | 3.18 III | 3.18 III | 3.18 III | 3.18 III | 3.18 III |
| 2.96 IV | 2.96 IV | 2.96 IV | 2.96 IV | 2.96 IV | 2.96 IV |
| 2.58 III | 2.58 III | 2.58 III | 2.58 III | 2.58 III | 2.58 III |
| 2.46 IV | 2.44 V | 2.46 IV | 2.46 IV | 2.46 IV | 2.46 IV |
| 2.40 IV | | 2.40 IV | 2.40 IV | 2.40 IV | 2.40 IV |
| 2.28 V | 2.26 IV | 2.28 V | 2.28 V | 2.28 V | 2.28 V |
| 2.15 V | 2.11 VI | 2.15 V | 2.15 V | 2.15 V | 2.15 V |
| 2.01 IV | 1.99 VI | 2.01 IV | 2.01 IV | 2.01 IV | 2.01 IV |
| 1.82 V | 1.81 VI | 1.82 V | 1.82 V | 1.82 V | 1.82 V |
| 1.67 V | 1.67 VI | 1.67 V | 1.67 V | 1.67 V | 1.67 V |

| | | | | | |
|----------|----------|----------|----------|----------|----------|
| 1.54 IV | | 1.54 IV | 1.54 IV | 1.54 IV | 1.54 IV |
| 1.51 III | 1.51 III | 1.50 III | 1.50 III | 1.50 III | 1.50 III |
| | | 1.46 VI | 1.46 VI | 1.46 VI | 1.46 VI |
| 1.38 V | 1.37 VI | 1.38 V | 1.38 V | 1.38 V | 1.38 V |
| | | | 1.35 VI | 1.35 VI | 1.35 VI |
| | | | 1.33 VI | 1.33 VI | 1.33 VI |
| 1.30 IV | | 1.30 IV | 1.30 IV | 1.30 IV | 1.30 IV |
| 1.26 V | 1.25 VI | 1.26 V | 1.26 V | 1.26 V | 1.26 V |
| | | 1.22 VI | 1.22 VI | 1.22 VI | 1.22 VI |
| 1.20 VI | 1.20 VI | 1.20 VI | 1.20 VI | 1.20 VI | 1.20 VI |
| 1.19 VI | 1.18 VI | 1.18 VI | 1.18 VI | 1.18 VI | 1.18 VI |

* Heated for 30 minutes at 600°C.

§ i: intensity, II: strong, III: Medium, IV: Weak, V: Very weak,
VI: barely visible, (: Reflection broadened.

Table 6. X-ray diffraction data of Ca-clay ($<2\mu$) saturated with ethylene glycol.

| 403 d(Å) i§ | 403(0.1) d(Å) i§ | 404 d(Å) i§ | 405 d(Å) i§ | 406 d(Å) i§ |
|----------------|---------------------|----------------|----------------|----------------|
| 10.2 IV | 9.5 IV | 10.2 IV | 10.2 IV | 10.2 IV |
| 7.2 V | 7.2 V | 7.2 IV | 7.2 IV | 7.2 IV |
| | 5.70 V | | | |
| | 4.98 VI | | | |
| | 4.39 II | | | |
| 4.21 III | | 4.21 III | 4.21 III | 4.21 III |
| 3.59 VI | 3.57 V | 3.59 VI | 3.59 VI | 3.59 VI |
| 3.35 II | 3.36 VI | 3.35 II | 3.35 II | 3.35 II |
| | 3.01 VI | | | |
| 2.54 IV | 2.55 III | 2.54 IV | 2.54 IV | 2.54 IV |
| 2.45 IV | | 2.45 IV | 2.45 IV | 2.45 IV |
| | 2.33 IV | | | |
| 2.29 V | | 2.29 V | 2.29 V | 2.29 V |
| 2.22 VI | | 2.22 VI | 2.22 VI | 2.22 VI |
| 2.13 VI | | 2.13 VI | 2.13 VI | 2.13 VI |
| 1.98 V | 1.96 VI | 1.98 V | 1.98 V | 1.98 V |
| 1.81 III | 1.79 | 1.81 III | 1.81 III | 1.81 III |
| 1.67 IV | 1.67 VI | 1.67 VI | 1.67 VI | 1.67 VI |
| | 1.65 | | | |
| 1.54 III | | 1.54 III | 1.54 III | 1.54 III |

| | | | | |
|----------|----------|----------|----------|----------|
| 1.50 III | 1.49 III | 1.50 III | 1.50 III | 1.50 III |
| 1.45 V | | 1.45 V | 1.45 V | 1.45 V |
| 1.38 III | | 1.38 III | 1.38 III | 1.38 III |
| 1.35 V | | 1.35 V | 1.35 V | 1.35 V |
| 1.28 V | 1.29 V | 1.28 V | 1.28 V | 1.28 V |
| 1.25 V | | 1.25 V | 1.25 V | 1.25 V |
| 1.23 VI | 1.23 V | 1.23 VI | 1.23 VI | 1.23 VI |
| 1.20 IV | | 1.20 IV | 1.20 IV | 1.20 IV |
| 1.18 V | | 1.18 V | 1.18 V | 1.18 V |
| 1.15 V | 1.15 V | 1.15 V | 1.15 V | 1.15 V |
| 1.08 V | | 1.08 V | 1.08 V | 1.08 V |
| 1.05 V | | 1.05 V | 1.05 V | 1.05 V |
| 1.04 V | | 1.04 V | 1.04 V | 1.04 V |
| 1.01 V | | 1.01 V | 1.01 V | 1.01 V |

§ i. Intensity, II: Strong, III: Medium, IV: Weak, V: Very weak, VI: Barely visible, (: Reflection broadened.

In the Nyuzen soil, illite is readily identified by the strong or medium lines at 10.0, 4.47-4.49, 3.34, 2.58, 2.39-2.40, 1.50-1.51 Å, and others. The major component in all of these clays is illite. The 15.1 Å basal spacing is due to chlorite, because it was remained after treating with ammonium ions and it gave a line at 14.2 Å after heating for 30 minutes at 600°C. As a weak line at 7.16 Å was decomposed by the heat-treatment, some kaolin mineral is present in a small amount. Gibbsite was also identified by a characteristic line at 4.84 Å. Besides these minerals, a small quantity of feldspar is also present.

The $<2\mu$ clay fractions of the Yokita soil contain appreciable illite and quartz, and some kaolin throughout the profile. Quartz is also noticed in the $<0.5\mu$ clay fraction, but no longer in the $<0.1\mu$ clay. The patterns have most lines of illite (dioctahedral) (2), but the order of intensity and the spacing of some lines are a little different from illite.

DIFFERENTIAL THERMAL ANALYSIS

The differential thermal curves of the clay fractions ($<2\mu$) are shown in Figure 1. The general similarity can be observed among all the curves from the Nyuzen profile, indicating that

there are no marked differences in the mineralogical composition among the horizons of the profile. In the Yokita soil the result is identical.

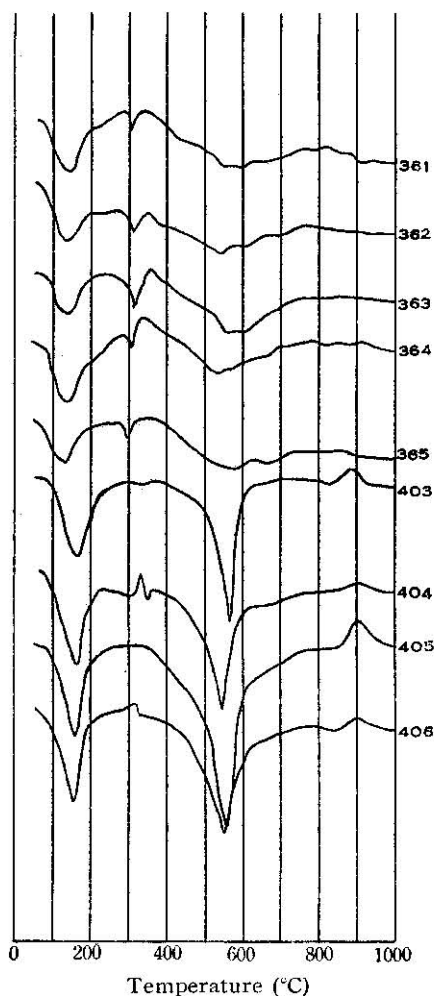


Fig. 1. Differential thermal curves of the Na-clays ($<2\mu$).

An endothermic peak of the Nyuzen soil at about 310°C . is probably caused by hydrated oxides of iron or aluminium, probably gibbsite as the x-ray analysis had indicated. A broad endothermic reaction having a peak in a range $530\text{--}600^{\circ}\text{C}$. is attributed to illite. Chlorite, identified by the x-ray analysis, may be responsible to a certain degree for this and some faint exothermic reactions in the region of $750\text{--}900^{\circ}\text{C}$.

The differential thermal records of the clay fractions from the Yokita profile show two distinctive intense endothermic reactions at $550\text{--}560^{\circ}\text{C}$. and $150\text{--}160^{\circ}\text{C}$. These curves bear some resemblance to the curve of hydrated halloysite, but the feature of the exothermic peak at the temperature between 900°C . and $1,000^{\circ}\text{C}$. marks the latter off from the former. An endothermic reaction just before the exothermic peak at about 900°C . and the dilatory endothermic reaction having a peak

at about 550°C . are also different from those of hydrated halloysite. These properties suggest that the predominant mineral of the clay fractions is an intermediate between illite and montmorin, perhaps degraded illite. Quartz was clearly recognized by the x-ray

analysis, but the endothermic reaction of quartz is barely observed in the thermal curve. The slight endothermic reaction of quartz at 573°C. may be cancelled by a very steep slope on the recovery of the endothermic reaction at the 550–560°C. peak.

DEHYDRATION ANALYSIS

The clay samples were continuously heated at a rate of 2°C./min., and the loss in weight was recorded at successively higher temperatures till at 900°C. The curves thus obtained are shown in Figure 2. Two curves differ from each other in shape. The clay fraction of the Yokita soil has two distinctive dehydration reactions. One is a loss of water at temperatures below 100°C.,

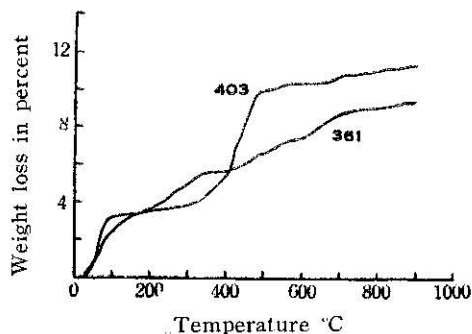


Fig. 2. Dehydration curves of the Na-clays (<2 μ).

and the other is at about 320°C. to 480°C. The former is undoubtedly due to the adsorbed water and the latter is ascribed to lattice OH ions passed off as H₂O. The general shape of this curve may appear to be similar to that of kaolin, but the starting temperature of the second reaction is too low for kaolin. It shows that the mineral has many OH ions capable of desertion at various temperatures between 320°C. and 480°C. Although any decisive identification of clay mineral is not introduced from the curve, the result is not contradictory to that from the x-ray and the differential thermal analyses.

No distinguished dehydration reaction is observed in the curve of the clay fraction of the Nyuzen soil. The curve—apparently not due to kaolin or montmorin—looks very much like the curve of illite (4).

CHEMICAL ANALYSIS

Chemical composition and cation-exchange capacity of the Na-clays ($<2\mu$) are shown in Table 7. Generally speaking, iron content is very low in all of the clay samples examined as compared with an average figure of that content in soil colloids of alluvial soils in Japan (5). It can be observed that the iron content in per cent of the fine earth is rather more than that of the

Table 7. Chemical composition of Na-clays ($<2\mu$).

| | | Nyuzen soil | | | | | Yokita soil | | | |
|---|-----|-------------|--------|-------|-------|-------|-------------|-------|-------|-------|
| | | 361 | 362 | 363 | 364 | 365 | 403 | 404 | 405 | 406 |
| SiO ₂ | (%) | 48.32 | 45.36 | 45.88 | 46.18 | 42.40 | 55.04 | 50.32 | 54.68 | 58.93 |
| Al ₂ O ₃ | (%) | 24.48 | 26.85 | 25.55 | 25.40 | 27.71 | 24.05 | 26.41 | 24.93 | 22.17 |
| Fe ₂ O ₃ | (%) | 4.16 | 5.59 | 4.67 | 4.41 | 5.46 | 2.10 | 5.70 | 2.45 | 2.01 |
| MnO | (%) | 0.08 | 0.08 | 0.40 | 0.11 | 0.24 | 0.17 | 0.22 | 0.18 | 0.11 |
| CaO | (%) | 2.66 | 2.48 | 2.32 | 2.18 | 2.26 | 1.10 | 0.85 | 0.61 | 0.56 |
| MgO | (%) | 4.51 | 4.77 | 5.10 | 4.81 | 4.87 | 0.75 | 0.87 | 0.76 | 0.87 |
| K ₂ O | (%) | 5.14 | 5.17 | 4.99 | 4.69 | 5.31 | 1.92 | 1.58 | 2.21 | 1.95 |
| TiO ₂ | (%) | 0.82 | 0.82 | 0.86 | 0.80 | 0.85 | 0.64 | 0.61 | 0.58 | 0.64 |
| P ₂ O ₅ | (%) | 0.08 | 0.06 | 0.12 | 0.11 | 0.06 | 0.06 | 0.06 | 0.03 | 0.06 |
| IL ₂ O(—) | (%) | 5.82 | 6.30 | 6.80 | 6.58 | 6.96 | 7.16 | 7.04 | 7.24 | 6.08 |
| H ₂ O(—) | (%) | 3.01 | 2.94 | 3.13 | 3.02 | 3.25 | 4.11 | 3.65 | 3.82 | 3.48 |
| Total | (%) | 99.08 | 100.42 | 99.82 | 99.29 | 99.37 | 97.10 | 97.31 | 97.49 | 96.86 |
| Molecular ratio (SiO ₂ /Al ₂ O ₃) | (%) | 3.35 | 2.87 | 3.05 | 3.09 | 2.60 | 3.88 | 3.23 | 3.72 | 4.51 |
| C. E. C. (m.e./100 gm.)* | | 27.8 | 25.5 | 25.5 | 25.5 | 25.9 | 37.2 | 33.4 | 31.9 | 29.5 |

* Cation-exchange capacity (oven dry basis).

clay fraction of the same earth. This fact suggests that colloidal iron being produced by weathering of primary minerals has been severely leached from the soil. Manganese is also very low in all clays, particularly those of the surface soils.

The clays in the Nyuzen soil contain large quantities of MgO and K₂O (about 5 per cent in either case), and high CaO content (about 2.5 per cent). This high K₂O content is attributed to the presence of a large amount of illite, and this conclusion agrees with that from the differential thermal, x-ray, and dehydration analyses above-mentioned. The content of illite is estimated to be about 80 to 90 per cent of the clay fraction on the basis of

per cent K_2O in illite (6 per cent). High MgO content is probably due to the presence of illite and chlorite, while that of CaO is partially caused by the presence of plagioclase.

The clay fractions of the Yokita soil are characterized by high amounts of SiO_2 and K_2O , fairly high quantities of MgO and CaO , and very low Fe_2O_3 content. A part of SiO_2 is attributed to the presence of quartz which is confirmed by the x-ray analysis. Considerably high K_2O content suggests the presence of illite or its relatives. However, granted that all K_2O is a constituent of illite (K_2O : 6 per cent), its content is estimated to be only about 25-35 per cent in the clay fractions.

Cation-exchange capacity of the clay fractions from the Nyuzen profile is relatively low, and it is nearly equal to that of illite (4). The clays of the Yokita soil are characterized by moderate cation-exchange capacity (30-37 m.e. per 100 gm.).

ETHYLENE GLYCOL RETENTION

Amounts of ethylene glycol retained by the clay fractions are given in Table 8. The internal surface areas of the clays of the Nyuzen soil are rather small (48-65 sq. m. per gm.). The clays separated from the Yokita soil have moderate surface areas which are about twice as large as those the former soil.

Table 8. Ethylene glycol retention by Ca-clays ($<2\mu$).

| Sample number | Ethylene glycol retention after 24 hours | | | Internal surface |
|---------------|--|------------------|------------|------------------|
| | Untreated | Heated at 600°C. | Difference | |
| | mg./gm. | mg./gm. | mg./gm. | sq. m./gm. |
| 361 | 36.9 | 20.4 | 16.5 | 53.2 |
| 362 | 43.1 | 26.3 | 16.8 | 54.1 |
| 363 | 46.2 | 31.3 | 14.9 | 48.0 |
| 364 | 43.1 | 23.0 | 20.1 | 64.8 |
| 365 | 46.1 | 29.2 | 16.9 | 54.5 |
| 403 | 61.7 | 28.1 | 33.6 | 108.3 |
| 404 | 49.1 | 20.5 | 28.6 | 92.2 |
| 405 | 52.7 | 17.1 | 35.6 | 114.8 |
| 406 | 44.7 | 10.4 | 34.3 | 110.6 |

ELECTRON MICROSCOPY

Electron micrographs of the clays ($<2\mu$) are shown in Figures 3 and 4. The sample from Nyuzen has particles somewhat rounded in various sizes, but in general with irregular shapes. Besides these particles it has thin plates and a few elongated particles.

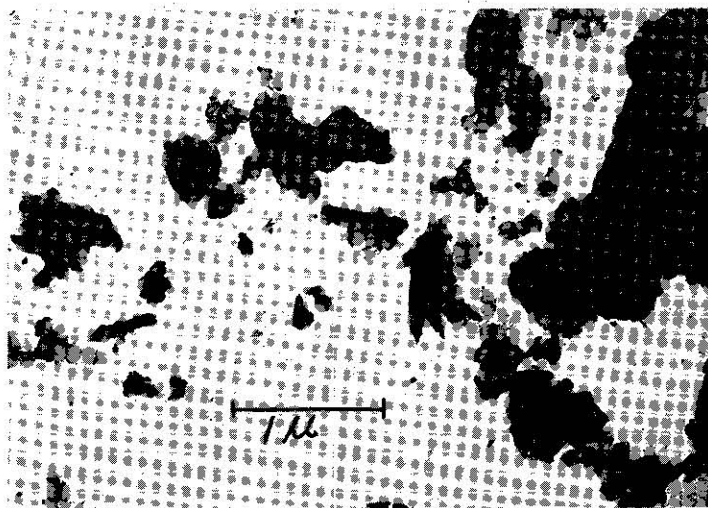


Fig. 3. Electron micrograph of Ca-clay ($<2\mu$) of Nyuzen soil 361.



Fig. 4. Electron micrograph of Ca-clay ($<2\mu$) of Yokita soil 406.

A considerable number of clay particles of the Yokita soil look like flakes—having irregular but well-defined outlines and a uniform thickness. A few elongated tubular particles indicating hydrated halloysite or halloysite and a very few large skeletons of diatoms were also found in the electron micrographs of the Yokita soil. Although it is not clear what mineral composes the thin flakes in the Yokita soil, they are a certain mineral having a layer lattice and considerable amounts of lattice OH ions and K ions. It is quite probable that they are degraded illite.

SUMMARY AND CONCLUSIONS

The soil samples examined were taken from two so-called degraded paddy fields in Toyama and Kagawa prefectures. One is an alluvial soil deposited by the Kurobe River and mainly derived from weathered materials of granites and gneisses. The other is also an alluvial soil derived from weathered granites and Cretaceous siliceous sandstones. Clay fractions less than 2 microns in effective diameter were separated from the soil samples after removing organic matter by treatment with H_2O_2 , and were examined by the thermal, chemical, x-ray, and other methods.

The Nyuzen soil was found to have predominant illite in the clay fractions by the x-ray and chemical analyses. These results were confirmed by the differential thermal and dehydration curves and other methods. The illite amount was estimated to comprise at least 80 per cent of the clay fractions on the basis of per cent K_2O in illite. The clay also contains chlorite, gibbsite, feldspar, and kaolin in small amounts.

It was noted that there was an abundance of degraded illite in the clay fractions of the Yokita soil with some quartz and a few kaolin and diatom particles.

The degraded paddy soils examined contain illite or degraded illite as a main clay mineral, having a little iron content, low cation-exchange capacity, and a small surface area. It, however, will be premature to conclude that these minerals are a general characteristic of the degraded paddy soil, because the number of the soils examined were too few to accept the results as common fact.

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