CLAY MINERALS IN A GLEI-SOIL I. INVESTIGATIONS BY CHEMICAL ANALYSIS, D.T.A. AND X-RAY DIFFRACTION

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CLAY MINERALS IN A GLEI-SOIL

I. INVESTIGATIONS BY CHEMICAL ANALYSIS, D.T.A. AND X-RAY DIFFRACTION

By

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Introduction

Clay minerals in soils are products formed and/or altered under influences of soil conditions and environmental actions of climates though the composing primary minerals play a marked role on them. It may be quite natural to consider that clay minerals in glei soils would be more or less different from those in well-drained upland soils and may possess some characteristic properties. However, unfortunately, there are but few reports on clay minerals in glei-soils, especially, with regard to their particular properties.

Almost all of the paddy fields in Japan have a glei-horizon at a relatively shallow depth from the surface, accordingly, glei-soils are considered to have important relationships genetically and in the sense of productivity with paddy soils. Studies on clay minerals in glei-soils were attempted and the soil in the fields of our university was investigated as representative of alluvial glei-soils.

Preparation of Sample

The glei-soil from which the soil sampled is an alluvium soil transported from the surrounding high lands of Tertiary and Quarternary sedimentary deposits. The layer at about 25~30 cm depth from the surface is a brown loam or a sandy clay and the next 20~25 cm is a clay loam with brownish color and scattered distinct mottlings of greyish blue and yellowish brown or orange yellow. The third layer at about 50~60 cm depth shows a bluish grey color and is composed of clay or sandy clay. The soil in the third layer was sampled and dispersed immediately using NaOH solution.

The suspension containing particle grains smaller than 2μ equivalent diameter was syphoned, fractioned into three portions each having diameters of $2.0\sim0.9\mu$, $0.9\sim0.3\mu$ and $<0.3\mu$.

After purification to exclude soil particles other than each required diameter the separated fractions were treated with H_2O_2, and freed from gels of SiO_2, Al- and Fe-hydroxides using the nacent hydrogen in the oxalate solutions. The fractioned clay samples were converted into H-clay for chemical analysis and into Ca-clay for D.T.A. and X-ray diffraction investigations. Then, all of the samples were stored in a desiccator to equilibrium with a vapor of 50 per cent R.H. After about two weeks storage, chemical analysis, D.T.A. and X-ray analysis were carried out because of the possible destruction or decisive alterations of clays during a long period storage. It became clear from the experimental results that caution must be given to store the sample in a saturated water vapor or in water from which air was driven out. In addition to three clay fractions, a fine silt fraction gaving a particle size from 2 to 5μ diameter was also analyzed.

Chemical Analysis

Total analysis of four fractions was carried out according to the ordinary methods of chemical analysis. Several components such as TiO_2, P_2O_5, MnO_2 and other minor elements were not determined because they are present only in negligibly small amounts. C.E.C. were measured using ammonium choride solution. The water content of both of H_2O^+ and H_2O^- were expressed as per cent of the weight of the sample heated at 260°C for 30 minutes.

The results are shown in Table 1. The conspicuous features which can be seen in Table 1 may be that the contents of divalent cations which should be considered to construct an octahedral layer of clay minerals such as Fe^{++} and Mg are very small. In considering the permanently reductive condition of the glei-horizon, it is of interest that the colloidal clay fraction contains

Table 1. Chemical constituents of the clays separated from a glei-soil.

	$2\sim5\mu$	$0.9\sim2.0\mu$	$0.3\sim0.9\mu$	$<0.3\mu$
SiO_2	68.84%	60.68	52.89	52.02
Al_2O_3	18.54	23.53	28.97	31.38
Fe_2O_3	3.10	3.56	3.41	3.50
FeO	0.78	1.24	1.41	0.57
MgO	1.14	1.62	1.92	0.80
CaO	0.31	0.45	0.14	0.16
K_2O	0.80	0.26	0.19	0.09
Na_2O	0.89	0.18	0.05	tr.
$(+)H_2O$	5.10	7.47	10.03	11.24
sum	99.50	98.99	99.01	99.81
$(-)H_2O$	5.47	6.05	8.17	11.65
C.E.C me./100g	24.7	29.9	39.5	48.1

Remark ; Per cent on the basis of the weight after heated at 260°C for 30 min.

such a low amount of Fe^{++} as 0.57 per cent. That the contents of MgO are as low as 1.1 or 1.9 per cent in the coarse fraction and only 0.85 per cent in the colloidal clays will be an indicative of the existence of very small amounts of Mg-bearing clay minerals as montmorillonite or some others. Another interesting point can be seen in that the contents of H_2O^+ (which can not be driven off when heated at 260°C for 30 minutes) are considerably high, especially, they are as high as 10 or 11.5 per cent in the case of the clays, $0.9 \sim 0.3\mu$ and that of $<0.3\mu$ fraction, respectively. A hygroscopic water and intralayer water of hydrated halloysite must have been lost completely by heating at the temperature 260°C. It is evident that there is no dropping of D.T.A. curve above 260°C till 350°C. Thus, the water content of 11.50 per cent of the colloidal clays is considered to have been lost from crystal lattices. If the cations relating with water in a crystal are Al, Fe^{3+}, Fe^{2+} and Mg, the total sum of the water corresponding to them amounts to 0.3535 mols according to the calculation by using the data in Table 1. On the contrary, the amounts of water lost above 260°C reaches 0.6389 mols. The excess of 0.2854 mols should be present in crystals in the form of water molecules. However, they also contain relatively large amounts of H_2O^-. This will indicate hygroscopic water in clays. Then, it follows that the clays would contain high amounts of highly active clays, if not so, there may exist an intra-layer water like those contained in hydrated halloysite or vermiculite. With regard to this point another report will be given in Part II. More or less higher amounts of MgO in the two coarser clays are considered to be due to the contamination of relatively higher amounts of chlorite minerals as explained later. The SiO_2/R_2O_3 ratios of the two finer clays are considerably low such as 2.90 and 2.63 in the cases of $0.9 \sim 0.3\mu$ and $<0.3\mu$ fractions, respectively. From these feagures we can consider that they would contain large amounts of kaolinite group clays, especially hydrated halloysite and/or dehydrated halloysite, however, in the colloidal clays there is a rather minor amount of them, at least, those in the form of separate crystal grain. This will be discussed in the next report.

The Results of D.T.A.

The experiments of D.T.A. were carried out at the heating rate of 10°C per minute. The results are shown in Fig 1. All four fractions show two prominent endothermic and an exothermic peaks at nearly equal temperatures. The first endothermic peak occurs at the temperature 135° to 145°C although the peak temperature becomes higher as the grain size decreases. The second endothermic peak appears in the range of the temperatures between 545° and 555°C. The depth of both of the first and second endothermic peaks becomes smaller as the particle size increases, however, the decrease of the peak depth

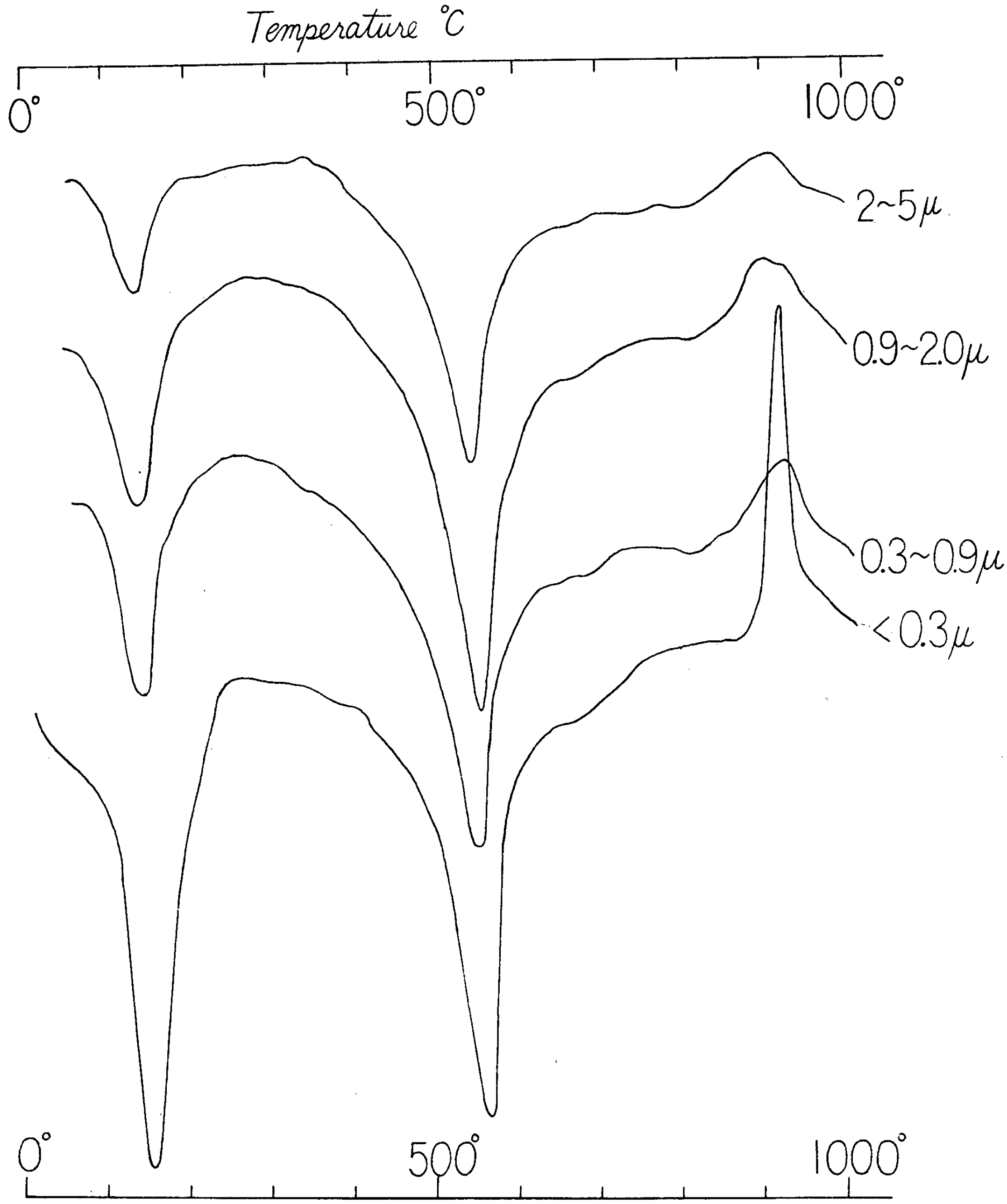


Fig. 1. D.T.A. of silt and clays separated from a glei-soil.

is more prominent in the first endo-peaks than that of the second.

The shape of the three coarser fractions is quite similar to montmorillonitic clays which are obtained from paddy soils and were reported elsewhere by the writers. That the droppings of the endothermic curves of the coarser three are smaller is considered to be due to an increase of quartz contents in them. Consequently, we consider that a large part of the clays other than quartz in the coarser fractions is composed of montmorillonitic clays, though there may be minor amounts of kaolinite and/or halloysite accompanying with some chloritic minerals.

The exothermic peak occurred at the temperature range between 910° and 925°C. Three coarser fractions show quite similar exothermic peaks to one another but in the colloidal clays its shape is very sharp and high like that of halloysite though the peak temperature was very low. The general feature of the whole curve of the colloidal clays is nearly equal to that of hydrated halloysite. However, its C.E.C. is considerably high even when heated at 310°C for 30 minutes as 32.47 me./100 g.

From a consideration on the type of D.T.A. curve of the colloidal clays, we can say that, at least, their clays would practically be composed of those which are nearly equal to halloysite in chemical composition owing to the existence of gibbsite-like layers between 2:1 lattice type clays forming a mixed-layer type structure. However, their essential characters are differing from those of halloysite and, on the contrary, they rather retain their original characteristics of 2:1 lattice clay minerals. An important question remained why gibbsite-like layers between two 2:1 lattice clays do not lose their lattice-OH water or water molecules which are substituted for lattice-OH at a low temperature as 320°~330°C as that of pure gibbsite. In general, D.T.A. curve of gibbsite shows two subsidiary small endothermic peaks at about 250°~300°C and 525°C. The first small peak is considered to be due to the formation of boehmite. Therefore, when the amount of gibbsite present is very small, the first endothermic peak becomes quite small and may be indistinguishable but the main endothermic peak at 320°~330°C must appear clearly to a remarkable extent. In the present case we could not find any indication of these peaks. Here we consider the reason as such that gibbsite-like layers are somewhat differing from pure gibbsite because it seemed that there exist some water molecules which substitute the OH-groups of gibbsite as follows; $[Al(OH)_2H_2O]$. In the case of such gibbsite-like layers, when they are heated they would convert at first to the structure of pure gibbsite through the loss of two hydrogen atoms per 2 atoms of Al.

When a gibbsite-layer is formed by the loss of water molecules, there results a structure quite similar to those of dehydrated halloysite because gibbsite-layers are sandwitched between two crystals of 2:1 lattice clays. Consequently, when these mixed-layer minerals are heated at a temperature above 300°C, the reaction should resemble the thermal reaction when halloysite is heated. This may be considered to be a main reason why the D.T.A. curve of the clays shows a very strong endothermic peak at 545°C and a very sharp exothermic peak quite resembling halloysite occurrs at 910°C, although both of these peak temperatures are somewhat lower. Several uncertainities concerning the thermal reaction of mixed-layer minerals, especially, about the complex random styles of multicomponents and polyhydrated, remain for future works.

X-ray Diffraction

The Ca-saturated samples of a fine silt fraction and three clay fractions have been examined by an automatic recording Geiger Countering X-ray diffraction equipment. The radiation of Cu–K_α was used at 40 kV, scanning speed of 0.2 degree per minute. The results are given in Fig. 2.

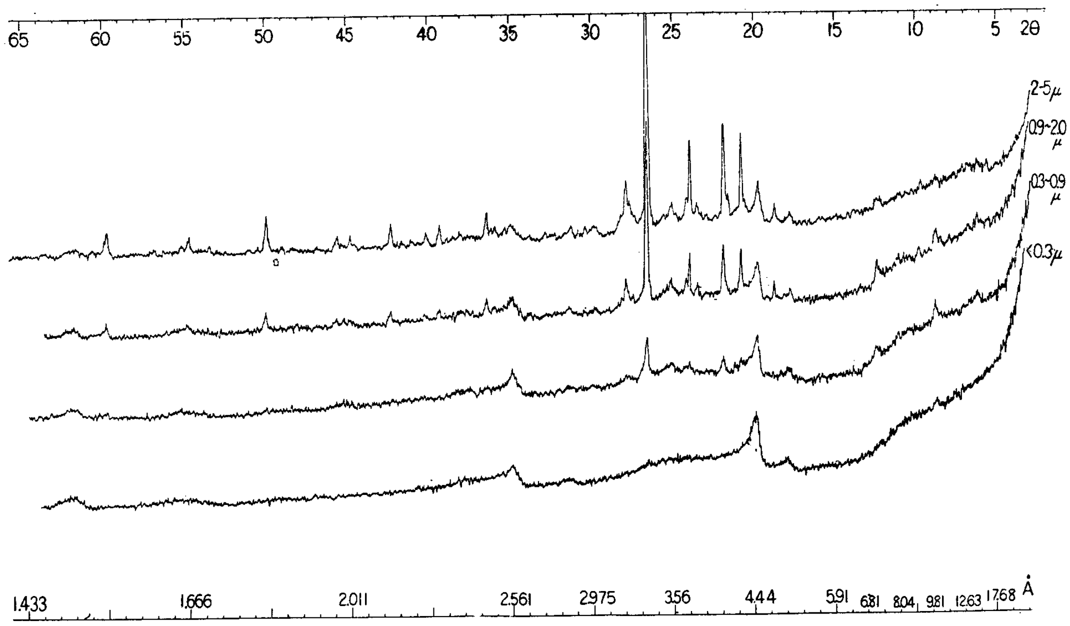


Fig. 2. X-ray diffraction of silt and clays separated from a glei-soil.

As can be seen in the case of the fine silt fraction and two coarser clay fractions numerous prominent diffractions correspond to that of quartz and cristobalite are observed, although they become less prominent as the grain size decreases. In the colloidal clays of <0.3μ they are almost negligible. The contents of quartz and cristobalite estimated by comparing the intensity of diffraction peak against the standard sample are as follows;

Fraction	Silt	Coarse clay	Medium clay	Colloidal clay
Diameter(μ)	2-5	2.0-0.9	0.9-0.3	<0.3
Amount of quartz and cristobalite(%)	25	12.5	2.0	0.0

The diffraction peaks of feldspars, 4.04, 3.78, 3.71, and 3.20 Å are clearly detected in both of silt and the coarse clay fraction, but they can be observed only scarcely in the case of the medium clays. However, as already shown in Table 1, the contents of all of CaO, K_2O and Na_2O are very small, accordingly, the amounts of orthoclase or plagioclase should be small. The total amount of feldspars would not exceed 10 per cent even in the silt fraction and may be less than 5 per cent in the coarse clay fractions, but the medium clays probably contains them only negligibly.

A general noticeable feature observed on all samples is the fact that there exists a diffused-like broad band of diffraction at the position of the range between 12° and 3.5° in 2θ.

The diffraction of the colloidal clays shows no distinguishable single peak in this range, though in the cases of the two coarser clays three distinct diffractions having a more or less high intensity above the band-type diffractions are recognized at about 7.15–7.20Å, 10.04Å and 14.25Å. In addition, four or five less intense peaks are detectable in the case of the clays 0.9–2.0μ, at the position of about 8.0–8.6Å, 9Å, 11.2Å, 13.0Å and 16Å. Such a tendency can also be seen in the case of the silt fraction but with far less intensity.

The diffractions at 7.15Å are the strongest in the coarse clay but the medium clays and the silt fraction show less intense peaks, and in the colloidal clays it was scarcely detectable. Accordingly, in thinking of both of the above facts and the peak at 1.485Å, kaolinite if present in all samples but even in the coarse clays it may be not so high in amount. The peaks of 7.20 or 7.38Å are also recognized but their intensity are less than 7.15Å, thus the content of halloysite and dehydrated halloysite is considered to be small, at least those which are present in a form of separated single crystals. The peaks at 10.0 or 10.04Å are more or less distinct, especialy in the cases of two coarser clays. The writer's opinion is that they can not be produced by illites because even in the case of the clays having the strongest peak, 0.9~2.0μ, its K_2O amount reaches only to 0.26 per cent. Consequently, a large part of the diffractions should be induced through either hydrated halloysite and/or the reflections of (002) and (003) of long spacing mixed-layer minerals.

The most characteristics of the diffraction features is a broad diffused-like diffractions, particulary remarkable in the case of the colloidal clays. They occur at three positions of from 7.6 to 17Å, from 3.35 to 4.4Å and 2.35 to 2.55Å, though an extremely weak one is observed at from 1.63 to 1.68Å. It must be noticed that in the lowest angle region the margin of the band-like diffraction can be observed to start at 6.8Å having less intensity but a marked diffraction can be seen from 7.2Å to a larger side. In the case of randomly interstratified mixed-layer minerals which having kaolinite or halloysite structure as a component show a broad band with its highly intense center at about 7.2Å. Thus the present case may not be if the same type but of a somewhat different one. We consider it must be a randomly mixed-layer with hydrated halloysite with montmorillonite type clays or with both of gibbsite-like layers and montmorillonite clays. The X-ray diffractions of the colloidal clays heated at 390°C will make it clear as shown in Fig 3. We have constructed this figure for the convenience of understanding. This was built through the procedure as follows. To determine a correct base line of X-ray diffraction is very difficult, especially where the region of the small angle of 2θ, however, we have intended to draw artificial base lines by free hand which are in common to both cases of non-heated and that heated at 390°C. Then the height of each diffraction peaks at each corresponding position of 2θ angle are translated on the same horizontal line in common. Heating at 390°C may be considered that it had given no decicive alteration or destruction on the clay structure but almost all of hygroscopic water and also those of inter-layer water could be driven off from the clays. Then the variation of diffraction peaks must be considered to express the variations of basal spacing brought about through the loss of inter-layer water. As can be seen from Fig 3, there occurred no prominent peak which highly intensified or that which was remarkably weakened. All of the diffraction peaks located in the broad band-like region from 7.75 Å to 17 Å became far less intense, while the peak of 7.36 Å became somewhat stronger. If one examined precisely there can be observed many individual peaks which were lost from non-heated clays but appeared on the curve of the heated. However, it is very difficult to interprete these variations accurately. If we note here several most evident diffractions in the non-heated clays they are 8.26, 8.60, 9.21, 9.60, 11.04, 11.62, 12.40, 16.0 and 19 Å. Almost all of the above diffractions became far less intense. On the contrary the diffraction peaks which became more or less

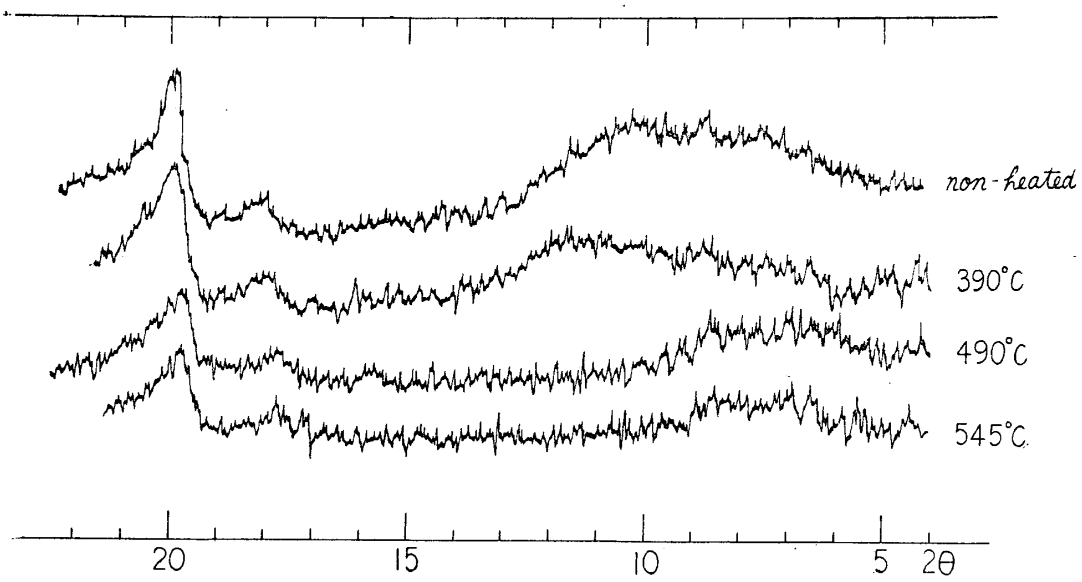


Fig. 3. X-ray diffraction of the colloidal clays heated at the various temperature.

highly intense are 7.90, 8.04, 8.20, 8.84, 9.70, 10.27, 11.34, 11.8, 12.6, 15.3 and 16.5Å.

Roy and Osborn reported that when halloysite is dehydrated at the temperature from 100°C to 450°C a diffraction peak appears at 7.17 Å with constancy but if they are dehydrated at a temperature too low for complete equilibrium to be dehydrated a diffraction peak does not occur at 7.17 Å but remains at 7.40 Å. In the case of the 0.9~2.0 μ clays the diffraction peaks at 7.15 and 7.3~7.4 Å did not become intensified by heating at 390°C, however, the colloidal clays showed a somewhat stronger peak at 7.40 Å, therefore, hydrated halloysite are considered to be present in this fraction although they may be not in so high an amount. Heating at 390°C induced a reduction of diffraction peaks over very broad range from 7.6 Å to about 17 Å. Among them the peaks at 8.3, 9, 11, 13~14, 16, and 17 Å are relatively distinct in the clays of 0.9~2.0 μ. The colloidal clays showed a continuous broad dropping of diffraction from 7.6 to 17 Å, though 10.4 and 14 Å are less remarkable. All these decreasings of diffraction intensity must be attributable to the decreasing of basal spacing as a result of the loss of intra-layer water. The diffraction peak at 10.05 or 10.15 Å can not be affected by heating at 390°C and remained with relatively small weakening. When these clays are heated at 545°C all of the peaks in the range from 7.15 to about 10 Å which persisted after heating at 390°C become markedly weak, however, the peaks between 10 Å and 14.2 Å remained almost unaltered. Tamura (1) interpreted these as an indication of minerals having chloritic nature. The intensified peaks at 14 Å by heating at 545°C can be recognized in the clays of 0.9~2.0 μ more distinctly. On clay minerals which having a basal spacing of 14 Å many workers such as Brown (2), White (3), Talvenheimo (4), Rich and Obenshain (5) and some others have presented discussions. Quite recently, Klages and White (6) reported an interesting example of mixed-layer minerals with gibbsite-like layer showing both of vermiculitic and chloritic characters. They clarified that these clays derived from illite by loss of their K ions and linking gibbsite islands between them. The diffraction peak at 14 Å of this clay collapses to 12.7 Å by heating at 350°C and to 10.3 Å by 550°C. However, in the present clays such characteristics could not be observed. A possibility of the presence of these clays can be considered but, as Hendricks and Teller (7) interpreted, when a large part of the clays is composed of mixed-layer silicate minerals having components of more than three different kinds of minerals they can not diffract any X-ray diffraction maximum. According to Sudo and Hayashi (8, 9), the broad band diffraction at a low angle region should be interpreted as an indication of long spacing clay minerals which are a randomly mixed-layer with two or more component minerals of either of the montmorillonite lattice (M-lattice), the kaolin lattice (K-lattice), the 14Å lacttice (G-lattice of gibbsite and pyrophillite), the lattice of 12.7 Å, and chlorite lattice of 14.5 Å. They also said that in Japan the so-called "acid clays" which is considered to be composed largely of random mixed-layer minerals of montmorillonite and kaolin minerals are considerably wide spread. They may be formed by alteration of tuff or tuffaceous sediments and acid volcanic rocks of Tertiary age. The parent materials of the present clays are like those inferred by Sudo and the X-ray diffraction feature examined is quite similar to that reported by him. D.T.A. curve of the present colloidal clays is similar but somewhat differs from that of Joshin clay which is cited by him.

According to the writers opinion, Sudo's hypothesis about long spacing minerals having gibbsite-like layers as their component and showing a broad band X-ray diffraction in the low angle region may be considered to be applicable as a general conclusion. However, a question arises as to which concerns the existence of hydrated halloysite. When we compare the two diffraction patterns of the non-heated clays and that heated at 390°C, as shown in Fig 3, the variation influenced by heating can be observed from the fact that all of the band type diffraction from 7.6 to 17 Å were weakened markedly including numerous individual diffraction peaks. But we could detect no remarkably intensified diffraction peak after heating at 390°C, especially those peaks correspond to dehydrated halloysite, accordingly, we have been unable to decide the presence of hydrated halloysite. Brindley and Goodyear (10) clarified that halloysite can behave somewhat similarily to montmorillonite in forming random interstratifications of different hydrates with different spacings. Also, Bradley has observed similar results. Unfortunately, these halloysite complexes were not examined by differential thermal analysis but the main effects may be presumed to occur as a variation in the intensity of the low temperature endothermic peak and as an induced endothermic peak at 500°C which was observed by Sand and Bates (11), however, if hydrated halloysite are intermixed only with a halloysite layer randomly mixed-layers of such type must show a distinct diffraction peak at 7.17 or 7.36 Å of halloysite when their interlayer water have been lost by heating. While in the present case we observed no marked peak of halloysite clearly intensified though more or less strengthened. This will indicate an impossibility of the existence of mixed-layered system simply composed of hydrated with dehydrated halloysite. Consequently we are forced to presume that a large part of hydrated halloysite and also halloysite would be present as a component of mixed-layer minerals with other minerals such as montmorillonitic 2 : 1 lattice type clays. A possibility to form such a type of mixed-layer minerals may not be undeniable when montmorillonitic minerals are advancing in their alteration process towards the formation of halloysite structure through linking with gibbsitic-layers under a water-saturated condition as in a glei-soil. In such a condition mixed-layers may be formed in numerous varied types of completely random style in which clays composed of two or more different kinds of components and also having multi-inter-layer sheets of water in them.

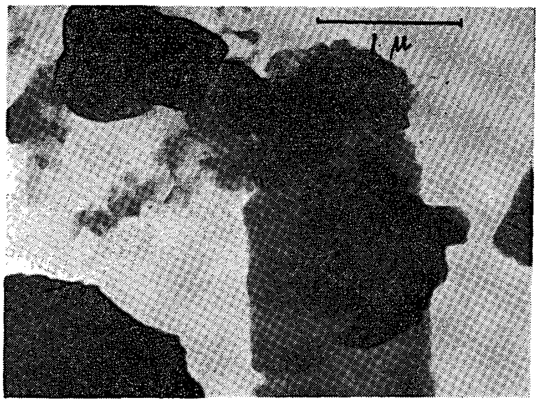
Electron Micrographs

The electron micrographs of three fractions of glei-soil clays are shown in Fig 4. As can be seen on the micrographs of all fractions, a large part of the particles show irregular outlines and thin platy shapes. We can also recognize some particles like tube-like type or rolled thin plates. The content of this tubes does not exceed 10 per cent. They are considered to be hydrated halloysite though we did not confirm that they are not poorly crystallized kaolinite. As it will be explained in Part II of this article, inspite of about 25 per cent of the colloidal clays is composed of hydrated halloysite and nearly half of the whole clays are mixed-layer minerals of montmorillonite with gibbsite-layer and/or halloysite layer, we can not observe so much amount of tublar or rolled-shape particles in the photograph. Such micrographs can not serve as proof that halloysite does not exist in a considerable extent. Halloysite may be able to exist in a plate shape especially linked with other plate-shaped crystals.

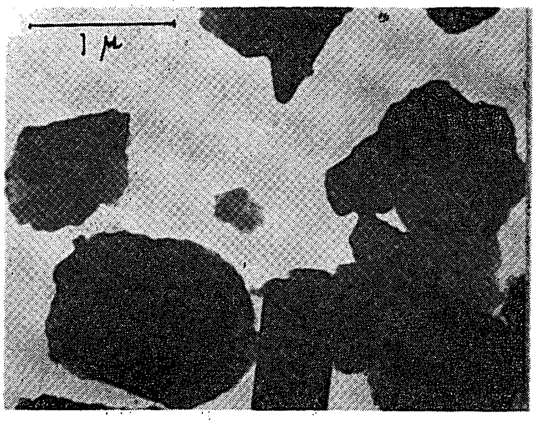
The present colloidal clays are considered to be in the alteration stage where almost all crystals had started from their original form of montmorillonitic structure to halloysitic or kaolinite type clays. There may be various alteration stages. Conditions in a soil medium, especially, such as glei-soil, are very variable and flexible. Accordingly, clays would vary in their form of construction of crystal structures and also in chemical compositions but they do not alter their crystal shapes so markedly because it seems natural that when a clay mineral is changed to another type under the least consumption of energy, alteration should be carried out so as not to increase their external surface areas, accordingly, the original crystal shapes are maintained and develop a form having their basal planes in common. This may be the main reason that the present clays show almost similar shape in electron micrographs. It may be reasonable to consider that the condition of soil such as glei-horizon present far favourable environments to them because almost all of the clays seemed to start from their origin of 2:1 lattice type clays and on the advanced stage of weathering large parts of their cations are freed, furthermore, activated Al-ions are supplied in solution. This may lead to the orientation of Al-ions in a sheet like layer on surfaces of 2:1 type clays and result to construct hydrated halloysitic structure and mixed layer minerals of gibbsite and 2:1 lattice clays.

Summary

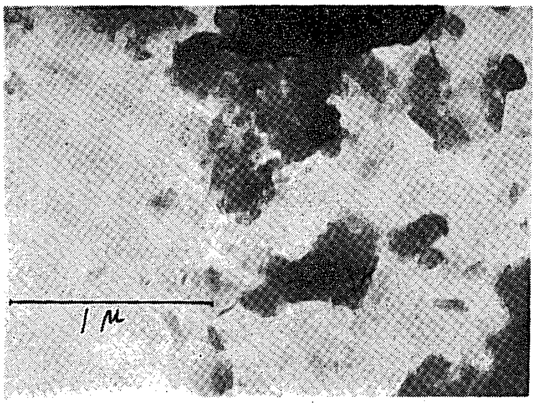
A fine silt fraction and three clay fractions of coarse, medium and colloidal



0.9∼2.0 μ



0.3∼0.9 μ



<0.3 μ

Fig. 4. Electron micrographs of the clay separated from a glei-soil.

grain size were separated from a glei-horizon of an alluvial soil. The fractioned samples were converted into H-saturated form for chemical analysis and into Ca-saturated samples for D.T.A. and X-ray diffraction experiments. The samples for electron microscope were used freshly prepared dispersion without any treatment.

According to the chemical analysis, all of the four samples contain very small amounts of CaO, MgO, K_2O, FeO and only a trace of Na_2O, however, they contain considerably high amounts of H_2O^+ and H_2O^-. Such a tendency is observed most marked in the case of the colloidal clays.

D.T.A. results showed highly prominent two endothermic reactions at 135°～145°C and 545°～555°C, a exothermic peak at 910°～925°C, especially, those of the colloidal clays are extremely sharp and deep, thus as a general shape it quite resembles to that of halloysite.

The results of X-ray diffraction investigations shows the presence of considerable amounts of quartz and cristobalite and small contents of feldspars, kaolinite, halloysite, and chloritic minerals in the silt and coarse clays, however, the colloidal clay fraction showed only prominent diffraction peaks at 4.4–4.5 Å and at 2.55 Å, less prominent of 1.68 Å and 1.448–1.449 Å although very broad band-like or diffused shape diffraction can be observed at four positions of from 7.6 Å to 17 or 19 Å, from 3.35 to 4.4 Å and from 2.35 Å to 2.55 Å, and less marked one of 1.63–1.68 Å. By considerations according to these results the writers conclude that the principal portion of the clays, especially the colloidal one, may be composed of a part of mixed-layer type minerals of hydrated halloysite with dehydrated halloysite and the other large portion are composed of dioctahedral 2:1 lattice type clays probably montmorillonitic or beidellitic clays, which are mixed-layered with gibbsite-like layer including intra-layer water sheets between them. Furthermore, we feel the possibility of the existence of mixed-layer mineral of 2:1 lattice clays with hydrated halloysite. Because X-ray diffraction patterns of the clays after heating at 390°C was weakened over almost all the range from 7.6–19 Å but we can not detect so marked increase of intensity at 7.1–7.4 Å and when heated at 545°C the diffractions at almost all of the region from 7.0 to 14 Å disappeared.

The figures of electron micrographs indicated that the most part of crystals are irregular disc or thin plate-shape having irregular boundaries but there exist a relatively small number, probably less than 20 per cent, of tube or rolled thinplate particles which seemed to be halloysite.

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