

## STUDIES ON CLAY MINERALS IN PADDY SOILS

著者	UCHIYAMA Nobuo, ONIKURA Yutaka
journal or publication title	Tohoku journal of agricultural research
volume	5
number	3
page range	159-176
year	1954-12-17
URL	<a href="http://hdl.handle.net/10097/29136">http://hdl.handle.net/10097/29136</a>

# STUDIES ON CLAY MINERALS IN PADDY SOILS

By

Nobuo UCHIYAMA and Yutaka ONIKURA

*Department of Agronomy, Faculty of Agriculture,  
Tohoku University, Sendai, Japan*

*(Received October 30, 1954)*

From the scanty of literatures dealing with clay minerals in paddy soils, it is noticed that some soil scientists regard these minerals to comprise chiefly halloysite or hydrous halloysite with minor amounts of kaolinite, dickite and/or nontronite. Their view being based upon the very low, 2.0 or there about, molar ratios of  $\text{SiO}_2/\text{R}_2\text{O}_3$ . However, such a view seems insufficient for understanding the soil forming process in paddy soils. We have reported(1) that the clay minerals found in a calcareous paddy soil (pH 7.0–8.2) are largely those of the expanding 2:1 layer lattice type, which possesses some characteristics similar to illite and montmorin-groups, especially to both of beidellite and nontronite. From the studies presented on the clay minerals in an acid paddy soil we are now able to contribute to the problem.

## **Samples used and experimental procedures**

The soil from which clays were separated is a paddy soil of the alluvial deposits at Iwanuma Town, Miyagi Prefecture, which consist of sediments transported by the Abukuma River. The surface layer consists of clay extending to about 25 cm depth, its color is dark gray with faintly brownish and greenish tint. This soil is underlain with a 2–5 cm thick clayey layer of white color and overlies a 30–50 cm peat layer.

The soil samples used for investigations, which are strongly acidic (pH 4.90), were collected from a depth of 15 cm from the surface. The fresh moist soil sample (not air dried) was digested by  $\text{H}_2\text{O}_2$  to remove the organic matter and then dispersed by NaOH solution at pH 8.0. At first, the suspension was separated by a siphon into two portions, one of which contained particles smaller than  $2\mu$ . The separated clay suspension was further separated into four fractions corresponding to the diameter of particles,  $<0.15\mu$ ,  $<0.6\mu$ ,  $0.6\text{--}1.0\mu$  and  $1.0\text{--}2.0\mu$ , by centrifuging. The time and number of volutions per minute were

adjusted precisely in each time to separate each of the above fractions. Then, each separate fraction was purified by centrifuging repeatedly to remove the particles finer than each limits. Purification of the portion of  $<0.6\mu$  to separate from the portion of  $<0.15\mu$  was abandoned. After the supernatant liquid became quite clear by ten times or more repeating of centrifugal purification, the precipitated clays were collected and treated with  $H_2S$  bubbles method after Drosdoff to remove Fe-hydrous oxide, and then digested with 2.0 per cent  $Na_2CO_3$  solution for 30 minutes to just boiling to remove the Si-gels and Al-gels. The clays thus treated were converted to H-clays by washing with dilute HCl solution and thenafter they were washed with distilled water to free the Cl ions. The suspension of the finest fractions was coagulated by NaCl before the treatments above mentioned. The four fractions of H-clays thus prepared were dried in room temperature and stored in a desiccator of 50 per cent relative humidity. These clay fractions were analyzed chemically according to ordinary methods.

For differential thermal analysis, 0.2000 gr of H-clays, weighted as accurately as possible, was used after a sufficient period in a desiccator to attain equilibrium. The heating rate was adjusted at  $10^\circ C$  elevation per min..

X-ray diffractions were investigated through the automatic recording micrometer with Geiger-Müller countering equipment. X-ray diffraction investigations were carried on four H-clay fractions separated according to particle size in a condition of water-adsorbed expanding state.

### Experimental Results

**Chemical Analysis.** The chemical constituents of the four fractions,  $<0.15\mu$ ,  $<0.6\mu$ ,  $0.6-1.0\mu$ , and  $1.0-2.0\mu$ , of the clays separated from a paddy soil are shown in the table 1. For comparison, there is also indicated an average composition of illite after Grim.

It can be seen that the contents of  $SiO_2$  increase with the increase of particle size but that of  $Al_2O_3$  and  $Fe_2O_3$  decrease. Barshad(2) has clarified that potassium fixed by 2:1 layer lattice minerals are relatively more easily replaced than potassium which is originally present in the contracted interlayer of micaceous layers of primary origin, that is the so-called native-potassium. We have recognized that the potassium in the fractions exceeding  $0.6\mu$  could not be reduced in any amount after one year elapsed under a condition of paddy planting, in the contrary, that in the finest fraction diminished to only 0.4 per cent. From this, potassium in the clays exceeding  $0.6\mu$  diameter should be considered to be present in a state of native-potassium or at least they may be in a state which is nearly equal to the structure of the original mica or illite. The content of potassium, however, increases with the increase of particle sizes and are considerably high, although even in the clays with the largest diameter is far

**Table 1.** Chemical constituents of the clay fractions separated from a paddy soil and that of illite after Grim et. al.

	< 0.15 $\mu$		< 0.6 $\mu$	1.0~0.6 $\mu$	2.0~1.0 $\mu$	Illite
	A	B				
SiO <sub>2</sub>	52.86	48.01	47.37	54.50	63.48	48.95
Al <sub>2</sub> O <sub>3</sub>	33.08	30.66	31.26	27.38	20.66	25.03
Fe <sub>2</sub> O <sub>3</sub>	} 8.99	} 8.28	} 7.41	} 5.51	} 5.29	9.03
FeO						1.61
MgO	0.91	0.83	0.61	0.57	0.45	3.10
CaO	0.08	0.07	0.05	0.06	0.40	0.29
Na <sub>2</sub> O	—	—	—	—	—	0.15
K <sub>2</sub> O	0.38	0.35	1.32	2.14	2.84	6.03
MnO	none	none	none	none	none	—
P <sub>2</sub> O <sub>5</sub>	none	none	none	none	none	—
TiO	—	—	—	—	—	0.51
(+)H <sub>2</sub> O	4.30	12.22	12.26	9.96	7.13	9.26
Sum.	100.60	100.42	100.29	100.12	100.25	101.89
C.E.C	—	74.5	52.8	46.4	34.9	50.0
SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub>	2.28	2.28	2.22	2.99	4.48	—

A : the material is analyzed after heated at 450°C for 2 hrs.

B : the material is the sample dried at 110°C.

C.E.C : Cation exchange capacity.

less than that of illite. We wish to call attention to the facts that the amounts of potassium, especially the fractions exceeding 0.6 $\mu$ , are higher than the contents of usual clay minerals and that the amount of 1.35 per cent in the clays of <0.6 $\mu$  became to as low as 0.45 per cent when analyzed after being laid one year under a paddy-planted condition with no-potassium fertilizer application. This may explain that the potassium content in the clays less than 0.6 $\mu$  is mainly in a difficultly exchangeable form which is unable to be expelled by washing with dilute HCl during preparation of clay samples for analysis but can be exchanged during a period of one year of strongly reduced condition of a water-lodging.

It is very noteworthy that the contents of MgO in all clay fractions are very small compared with ordinary or typical chlorite or vermiculite. From this fact it may be reasonable to consider that the clays which represent the principal portion of these all clay fractions would not be those of the clay minerals of typical trioctahedral type having high MgO content such as chlorite or vermiculite etc.

An interesting fact is that the clays finer than 0.15 $\mu$  have a very low silica : alumina ratio and silica : sesquioxides ratio, as 2.28. Furthermore the ratio of the fractions finer than 0.6 $\mu$  is still less. This means that in the clay fraction having their particle sizes between 0.15 $\mu$  and 0.6 $\mu$  there should exist clays of which SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is very low, that is 2.0 or less. Hitherto, it is generally

accepted that clays in paddy soils having such a low silica : alumina ratio are halloysite and that clay formation in paddy soil conditions is essentially such a process in which 1 : 1 layer type clay formation is predominant and accompanies the formation of some dickite or nontronite. From the reason that the water content of the finest clays of  $<0.15\mu$  is only 4.30 per cent when measured after heating at  $450^{\circ}\text{C}$  for two hours, the clays can not be halloysite but they should belong to the clays of 2 : 1 layer lattice type.

The coarser two fractions show distinctly X-ray diffraction lines of quartz as will be explained later. Accordingly, the reason of a relatively high Si : Al ratio of the coarser fractions should be due to the presence of quartz and, therefore, the clays other than quartz in these fractions are considered to be those which are nearly equal to the finer clays. An absence of quartz in the fraction less than  $0.6\mu$  and its existence in the coarser fractions which can be detected by X-ray diffraction studies as will be mentioned later, may be an indication that quartz formed in paddy soils may possess a diameter not less than  $0.6\mu$ .

We have discussed elsewhere(3) that soluble  $\text{SiO}_2$  in paddy soils is converted into insoluble forms during the period of stagnant condition from August to October, especially in the fraction of particle sizes between  $0.6\text{--}2.0\mu$ .

From the facts that the content of potassium in the clays less than  $0.6\mu$  has been reduced from 1.32 per cent to merely 0.4 per cent after one year and that a possibility of the presence of halloysite in this fraction may be expected, the principal portion of this clay fraction is considered to be quite the same as those in the clays of  $<0.15\mu$ .

The two coarser clays are considered to be similar types because the high amount of  $\text{SiO}_2$  and the low contents of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  may be interpreted by the presence of quartz which was detected through X-ray diffraction as will be mentioned later.

The relatively low values of potassium contents compared with that of illite and also somewhat lower values of C. E. C. of these two coarser fractions may be explained by that the coarser fractions have a greater thickness of particle unit formed by stratification of 2 : 1 layer lattice crystal structure in which K atoms serve as contracting force and that the large sizes of the particles, especially their thickness produced by stratification, will reduce their total surface area per unit weight of clays. Merely from results of chemical analysis of these clays it is impossible to interpret their precise features.

**Differential Thermal Analysis.** The three clay fractions used in the above chemical analysis were stored in a desiccator of 50 per cent R.H. vapor until equilibrium was attained. They were analysed through differential thermal analysis by heating at the rate of  $10^{\circ}\text{C}$  per minute. The results are shown in Fig. 1.

As can be seen from Fig 1, the three curves show quite similar shapes, and this is an indication that the clays in these three clay fractions consist of the

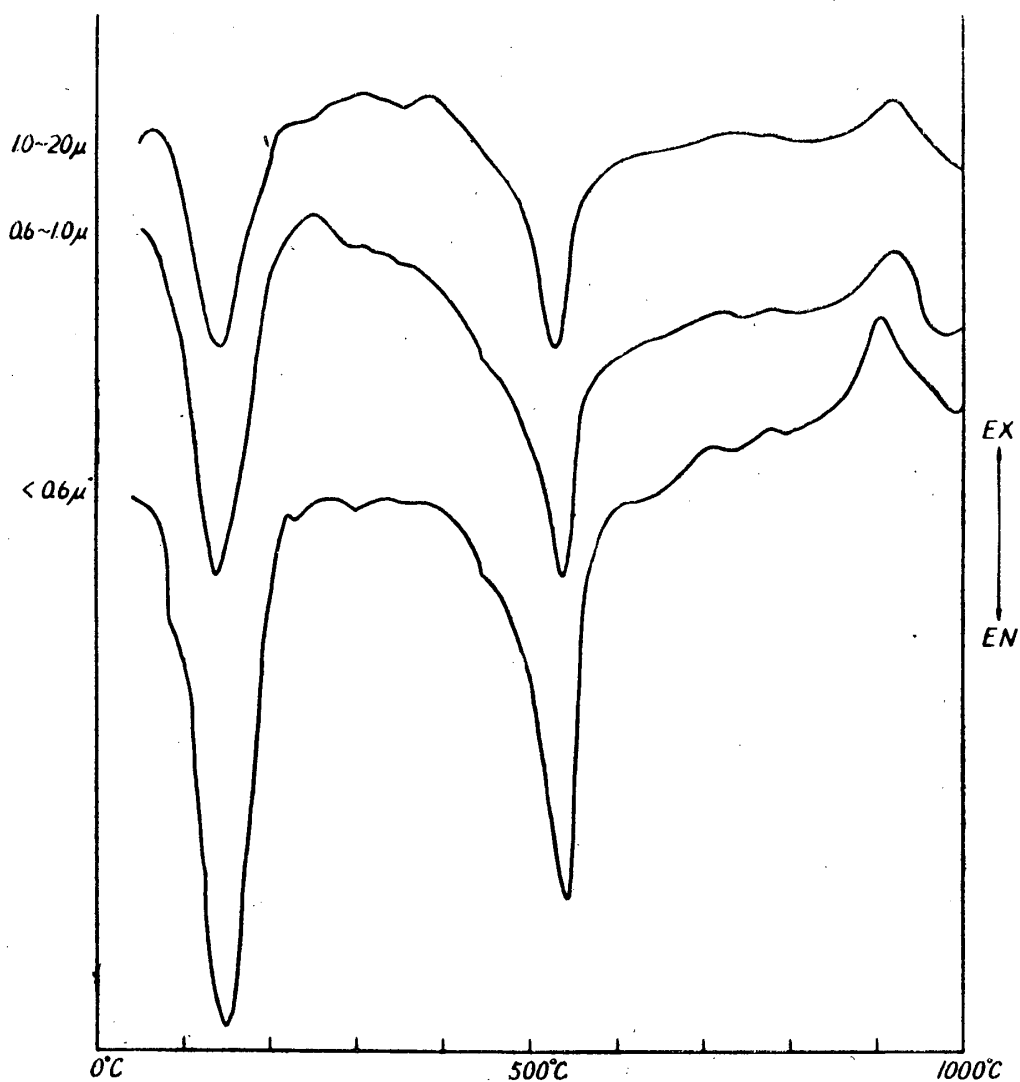


Fig. 1. Diagram of differential thermal curves of three portions of clays separated from a paddy soil.

same kind of clay minerals. The smaller peak depth of the second endothermic peaks in the case of the coarser particle sizes of  $0.6\text{--}1.0\mu$  and  $1.0\text{--}2.0\mu$  should be attributed to the less amount of the clay minerals owing to the presence of other clays such as halloysite or quartz. The similarity of the predominant clay minerals in the three fractions will be illustrated by X-ray diffraction investigations. As a whole, the second endothermic peaks of the three fractions are rather sharp and large compared with those of the typical illite and montmorin-group. The temperatures of the second endothermic peak which may correspond to the destruction of OH-groups in crystal lattice are all at  $530^{\circ}\text{C}\text{--}540^{\circ}\text{C}$ . This temperature is lower by about  $40^{\circ}\text{C}$  than halloysite or kaolinite and still lower than beidellite, montmorillonite or illite. In recent

years, it has become clear that clays of 2 : 1 layer lattice type in soils, especially montmorin group, show endothermic peak at about 530°C. Robertson(4) suggested that when the disorderiness in a crystal lattice increases, the temperature of the peak point of the principal endothermic peak curve will shift to the lower side of the temperature. Such a low temperature of the endothermic peak of soil clays would indicate the existence of a considerable high irregularity or disorder in crystal of soil clays. According to Grimshaw et. al. (5), the loss of water from crystal lattice of halloysite begins rapidly and abruptly at 400°C or slightly higher to 430°C and its endothermic peak may occur at 500°C. Although a general shape of the second endothermal peak of the finest fraction is quite similar to that of halloysite, if almost all or the larger part of the clays are halloysite, the clear high X-ray diffraction at 10 Å or at 7.1–7.4 Å must appear when they are exposed to the radiations of X-ray. However, we can not recognize such a characteristic diffraction of halloysite so distinctly, at least, in the case of the non-heated clays of the finest fraction. As will be explained later, more or less clear diffraction peaks at or near 7.1–7.3 Å can be detected in the case of the clays larger than 0.15 $\mu$ , especially, <0.6 $\mu$  or 0.6–1.0 $\mu$ . If a considerable amount of typical halloysite is present, the second endothermic curve may be divided into two peaks of 530–540° and 570°C or the curve must break at the point corresponding to 560 or 570°C. However, when the content of halloysite is relatively small as low as 10 per cent or less, we can not find out it's presence by the shape of a curve. According to Sand and Bates (6), the presence of a small amount of halloysite such as 10 per cent or less can not break an endothermic curve between 400 or 600°C. Therefore, we can not refuse an assumption that a relatively small amount of halloystie may exist in the fractions larger than 0.15 $\mu$ , but we can say from the results of X-ray diffraction that there is almost no halloysite in the fraction < 0.15 $\mu$ .

From the fact that the curve of the second endothermal peak begins to descend at 400°C and its curvature breaks at 450°C, we can say, at least, that OH groups which quite resemble that of halloysite or to those having gibbsite structure and can be set free by heating at 400°C or over to 450°C should be present. However, these OH groups should be present in forms other than that of individual halloysite or of particles having gibbsite-like structure.

An endothermic peak which occurs below 200°C is considered to represent a desorption of hygroscopic or adsorbed water on clay surfaces. Such a large endothermic peak depth shown by the clays here studied may be attributed to the very large amounts of surface areas of this clays.

The next important fact is that on the curves of all clay fractions there exist no distinctly observed endothermic peaks at or near 600°C. This is an indication of the absence of chlorite or at least an absence of individual or separated chlorite particles in an observable extent although they may be present as a member

of one of stratified layer, especially, as the clays having triocta-layer in their mixed-layers.

Many trials to utilize curves of differential thermal analysis for distinguishing or differentiation of clay minerals have been undertaken by some workers. That a shape of differential thermal curve is altered when the crystallinity of clays is varied was indicated by Grimshaw et. al.(7). Gruner (8) et. al. also suggested that it is changed as a result of impurity in clays. Bramao et. al.(9) also pointed out that it should be altered by both differences in particle size and degree of crystallinity. Murray(10) used a temperature range of endothermic peak, temperature at peak, and a peak depth as useful tools for distinguishing the degree of crystallinity. Of course, a shape of differential thermal curve and a depth of endothermic peak must be altered through many factors arising from the experimental techniques used and the inherent nature of clay itself. However, when a heating rate is maintained at a quite constant rate, say, at a rate of 10°C per minute through the entire range of investigation, and weights of samples used are always precisely equal in all operations as accurate as possible, in our experiments it was 0.2000 gr. and the packing technique is in quite the same manner, the ratio obtained between the magnitudes of the depth of the first and the second peaks may be used for distinguishing the different clay minerals from each other.

All clays possess their own characteristic adsorption capacities toward water molecules according to their own particle sizes, shapes of crystals, amount of charges on crystal surfaces, and cations adsorbed on their surface. Moreover, all clays possess their own characteristic features shown by a desorption of OH-groups from their crystal lattices. Thus, the ratios obtained when the depth (cm.) of the second endothermic peak ( $p_2$ ) divided by that of the first endothermic peak ( $p_1$ ) would show characteristic numerous values according to the kinds of clay minerals.

The ratios of several typical clay minerals thus obtained are as follows.

clay minerals.	ratio of two peaks, $P_2/P_1$ .
kaolinite	10.0
halloysite	1.1-1.56 or 2.60*
illite	1.00
montmorillonite	0.60-0.85
nontronite	0.2-0.5
clays from paddy soil	
1.0-2.0 $\mu$ .	0.84
0.6-1.0 $\mu$	0.75
<0.6 $\mu$	0.62

\*after Grim

The peak-depth ratios are not always quite constant because clays, especially soil clays, can not be prepared in a very pure state by fractionation, in addition,



soil clays are very complex and irregular in their forms of crystal structure. However, if sufficient precautions are given on operations of a series of differential thermal analysis, the ratios may serve as a tool for a distinguishing clay minerals. From the above values, the clays in this paddy soils can be considered to possess a montmorin character in them. Characteristic nature in the crystal lattice structure of clays may be shown on some portions of a differential thermal curve where a destruction of their crystal structure occurred. On the basis of this consideration, we intended to seek some characteristic features from the second endothermic peak curves. Bramao et. al (9) has already examined some clay minerals. However, he failed to find a clear relationship between ratios and kinds of clay minerals. Robertson (4) discussed on the assumption of Bramao. We consider that his failure may be attributed to his method which he selected because he used only one decline ratio obtained by comparing two declinations at the two turning points of a endothermic curve, to say, at the beginning of descendance of the endo-peak and at the terminal point of the ascending curve. Only one ratio of declination of a curve at merely such two points should obscure a distinct relationship, if present, through disturbances operated by many factors on the vicinity of these points. It is considered that the drop of temperature as the result of removal of OH-groups from crystal lattices must reflect the strength of bonding or linkage between OH-group and cations of crystal lattice such as Si, Al, Fe, Mg etc. which are linking to OH. Consequently, on the shape of curvature on both sides of the second endothermic-peak, characteristics of crystal structures could be found. Based on this assumption, we intended to construct the decline ratios as many as possible, for example, as a continuous form or an integral type on a whole range between a peak point and a base line. At first, a line perpendicular to the base line is drawn through the peak point on the second endothermic curve. Numerous points each of which are separated from each other by a constant distance, for example 2.5 mm or 5.0 mm, are marked on this perpendicular line from the peak point to the base line. Lines parallel to the base line which pass every point thus obtained are constructed. The lengths of width between the points of intersection of the parallel lines which dissect the curve and the perpendicular line are compared between the left-hand side and the right hand side. The ratios on the curve thus obtained,  $R_1, R_2, R_3, \dots$ , should be drawn on a graph from the peak to the base line. These are shown in Figs. 2 and 3. The values or the shapes of the graphs of this decline ratios show a particular figure representing a given clay mineral. When a clay fraction consists of a mixture of different kinds of clays the lines obtained by these ratios from the peak to the base line show a declined line in which short horizontal portions may appear, however, when clays consist from only one kind it becomes a straight horizontal line having no declined portion. The values of the decline ratios of several clay minerals are considered

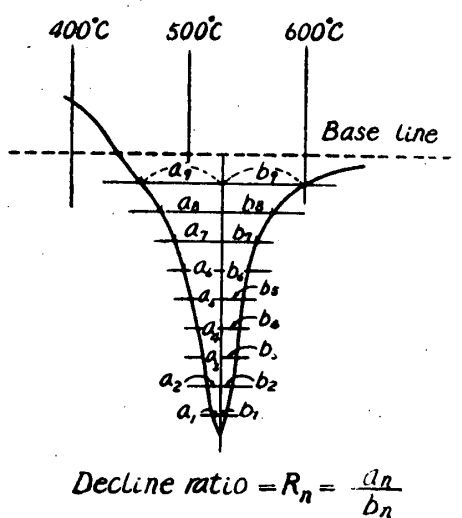


Fig. 2. Schematic representation of decline ratio of clay fraction 2.0-1.0 $\mu$  diameter.

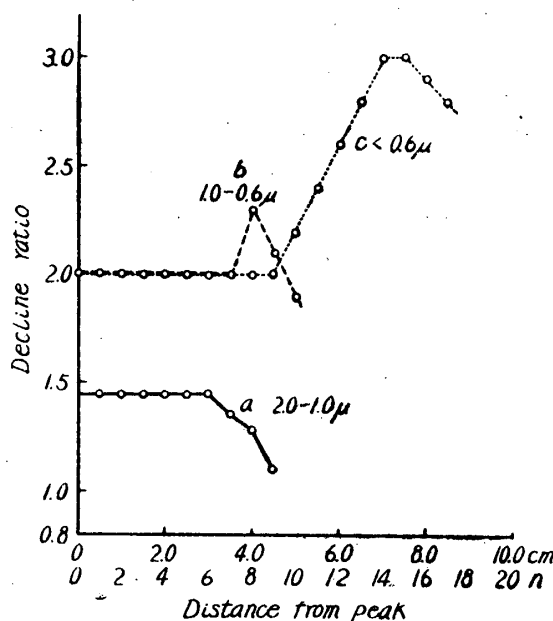


Fig. 3. Decline ratio graphs of three fractions of paddy soil clays.

to be as follows :

kaolinite	1.1-1.5
halloysite	3.0 or over
illite	1.0 nerally constant
montmorillonite	1.8-2.8
nontronite	0.7-0.8

The ratios of the clays studied here are presented in Fig. 3. From the curves in Fig. 3, it may be said that the largest clays, 1.0-2.0 $\mu$ , will be in an intermediate position between illite and montmorillonite, and that of 0.6-1.0 $\mu$  is in the range of montmorillonite. Although it possesses a part of the line declined upward which suggests the value of halloysite, this portion corresponds to the region of temperature below 450°C. The curve of the finest clays is 2.0 in the vicinity of the peak point but it also rises to 3.0 below a temperature of 450°C. Through an examination of this procedure the clays studied here also indicate the presence of montmorillonitic characters, but the presence of halloysite was not clear. Like the results of chemical analysis, the investigations through differential thermal analysis could not detect a precise feature of the clays although we could obtain some knowledge regarding on the nature of the clays.

**X-ray Diffraction Studies.** The samples used for X-ray diffraction investigations are the same three H-clay fractions; <0.6 $\mu$ , 0.6-1.0 $\mu$ , and 1.0-2.0 $\mu$  which were investigated by chemical analysis and differential thermal analysis mentioned above. In addition, we used medium silt fractions of

9–11 $\mu$  diameter which had been separated from the same paddy soil. Although the results of the microphotographs of X-ray diffraction powder patterns of the three clays are not shown here, we could make clear that they show rather small number of diffraction lines. Especially, those seen in the case of the clays <0.6 $\mu$  are quite similar to those of 2:1 lattice type clay minerals containing no line of other minerals. However, the clays of 0.6–1.0 $\mu$  and 1.0–2.0 $\mu$  diameters show somewhat distinct diffraction lines which correspond to quartz and cristobalite. Further, we can observe a broadening tendency of the lines and scattering features in the region of (d)-values from 15.5 or 16.5 Å to 4.5 Å and from 4.0 Å to 2.0 Å. As a general tendency, the feature of diffractions of the clays <0.6 $\mu$  seemed to resemble the clays from calcareous paddy soil on which we have discussed elsewhere. The diffraction patterns of the coarser two fractions show quite similar features except for those lines which correspond to quartz and halloysite. Therefore, the principal portion of these three fractions can be considered to be the same type of clay minerals. To acquire a more accurate knowledge on the clays and to clarify, if possible, the real meanings of the scattering and the broad band-like nature, we investigated these three clays and, in addition, H-clays smaller than 0.15 $\mu$ , and a medium silt fraction of 9–11 $\mu$  using the Automatic Recording Geiger-Müller Counting X-ray Spectrometer. The  $K\alpha_1$  radiation of copper was used. The procedure used were 42 kV, 40 mA, S.F. 64 and T.C. 4, 2°/min. The results are shown graphically in Fig. 4. In this figure the curve of (d), the clays <0.6 $\mu$ , is cut off in the region of a high angle owing to the failure of an investigation using the same procedure as that used for the other samples. Then we added the curve of the dotted line which was obtained by using the procedure of X-ray of 42 kV, 18 mA, and S.F. 32 and T. C. 4, 2°/min. We can observe clear indications of the presence of quartz in the samples of silt and two clays of 0.6–1.0 $\mu$  and 1.0–2.0 $\mu$ , but there is no such diffractions in the two clay fractions smaller than 0.6 $\mu$  and 0.15 $\mu$ . Furthermore, the prominent diffraction peaks at 4.10 Å and 3.20 Å are observed in the silt fraction and the two clay fractions of 0.6–1.0 $\mu$  and 1.0–2.0 $\mu$ . These distinct two peaks are slightly, about 0.05 Å, larger than the values of cristobalite given by Brindley. We inclined to consider that these peaks may be an indication of cristobalite rather than feldspars, however, the problem needs further study. From this we can consider that quartz in a clay fraction must mainly be formed by the new formation and their particle sizes should be larger than 0.6 $\mu$ . In addition, the presence of a small amount of 1:1 layer lattice mineral, probably halloysite, can be expected in the cases of the clays larger than 0.15 $\mu$  because only the clay <0.15 $\mu$  shows no distinct peaks of halloysite. The magnitude of halloysite particles newly formed, therefore, may be considered to be not smaller than 0.15 $\mu$ . One other point to be noticed is that the diffraction peak of mica or illite of 10 Å could not

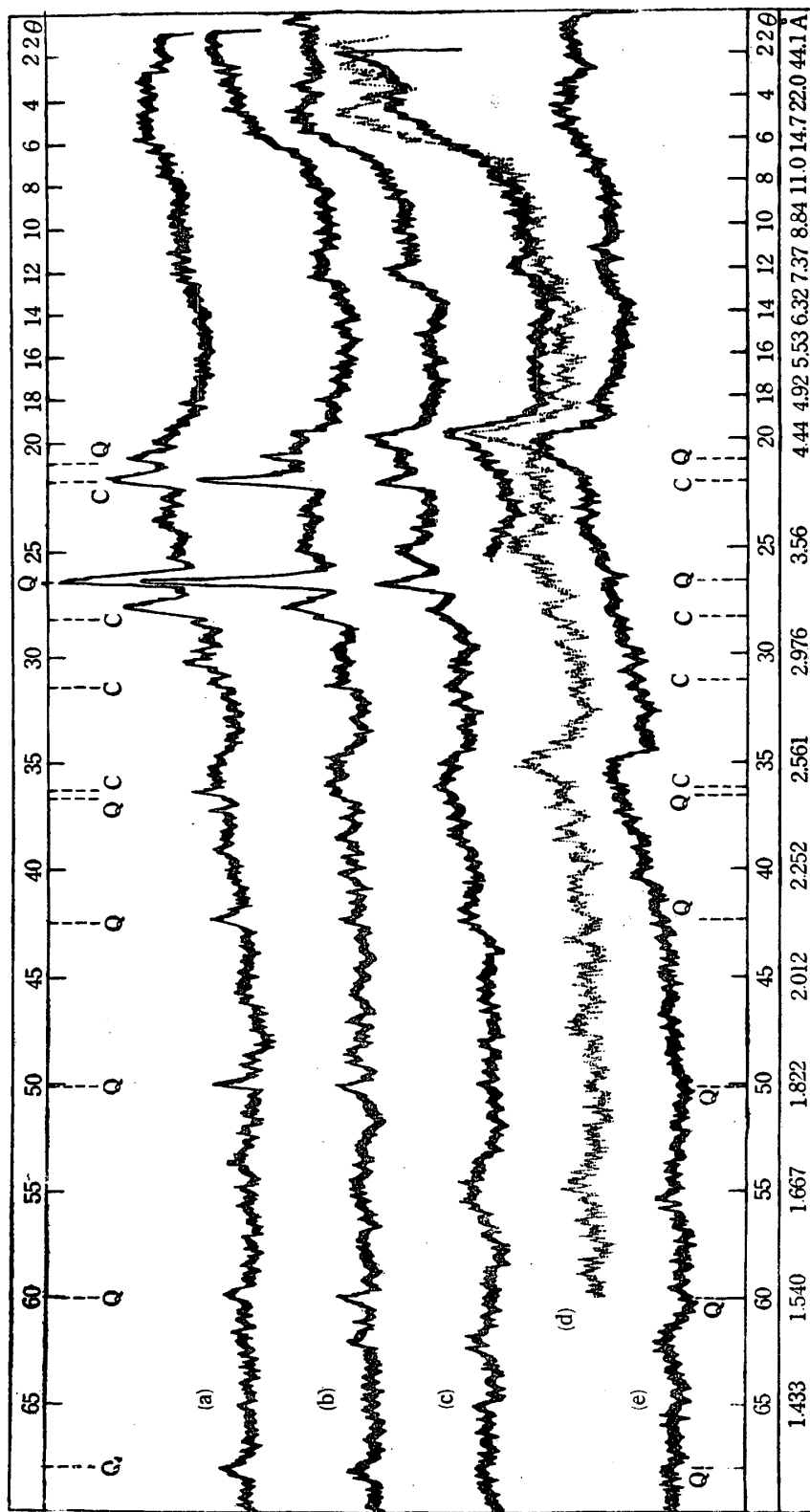


Fig. 4. X-ray diffraction patterns of medium silt fraction (9-11 $\mu$ ) and four portions of clays separated from a paddy soil. Symbols a, b, c, d and e designate samples of silt (a), clays of 2.0-1.0 $\mu$  (b), 1.0-0.6 $\mu$ , (c), smaller than 0.6 $\mu$  (d), and clays smaller than 0.15 $\mu$  (e), respectively. Q, denotes quartz, C, represents cristobalite.

be detected in any fraction so distinctly. From this we can say that there exist no mica-layer minerals as separated single particles.

A characteristic feature common to all clays is that a relatively high diffraction intensity occurred in the region from 15.4 Å to 25.5 Å, dissected into several small peaks although in the case of the larger particles the diffraction intensities are less. Furthermore, much higher basal diffractions such as 27 Å to 29 Å are supposed to exist. A particularly interesting feature shown by these clays is that many small peaks of reflections are scattered over almost the whole range, especially, in the portions of the small angle region several dissected small peaks are grouped. On the possibility of the occurrence of such separated peak-groups Jackson M. L.(11) already interpreted it as "preferential weathering" of micas. According to his theory and results of some others, these dissected series of peaks may be considered to occur from clays which are formed by the combination of two or three kinds of layer lattice minerals such as mica- and montmorin-layers or some others especially when they adsorbed different degrees of water on their surface such as mono-, di-, or tri-layers. From the points above mentioned, it may be most plausible to consider that the principal portions of all these clays would be a mixed-layer type or so-called stratified clay minerals. According to McEvan(12), the indices (060) which stands out in the neighbourhood of 1.50 Å of X-ray diffraction can be used to distinguish dioctahedral- from trioctahedral-mica or vermiculite because the position of this line varies only according to the structural composition of the crystal lattice and not to differences of the spacing between the crystal sheets. The dioctahedral-layer shows a line in the range of 1.49 or 1.52 Å, however, the trioctahedral layer at from 1.525 to 1.535 Å. The clays here studied have a line between 1.50 and 1.515 Å. There can be seen a diffraction peak at 1.54 Å which may be attributed to chlorite (1.53-1.56 Å), but when the clays are heated at 600°C no indication of increasing intensity of 14 Å peak could be recognized. In addition, there are present no peaks distinctly prominent at 7 Å, 3.5 Å and 4.7 Å of (002), (004), or (003) of chlorite. Consequently, the peak at 1.54 Å should be that of quartz, and we can say that no recognizable amount, if any, of trioctahedral-micas or chlorite exist or, at least, they should not be present in a state of individual separated particles. These deductions are supported by the concepts which have been mentioned from the results of our chemical analysis and differential thermal analysis.

In the case of the non-heated sample of the finest clays  $<0.15\mu$ , the relatively high diffraction peaks are observed in the region of (d)-values from 16.5 Å to 22.5 Å.

All of the peaks between 16.5 Å and 22.5 Å are grouped and give a considerably high intensity, although individual peaks are not necessarily so large. Although we can not measure their (d)-values quite accurately from these figures, such

grouped diffractions may not be a simple scattering but that they may be due to the actual presence of clays having large basal spacings which correspond to each diffraction peaks. With regard to the occurrence of clays having such large basal spacings no information or discussions have hitherto been offered except for a possibility of occurrence of clays with basal spacings of 28.5 Å. Notwithstanding the absence of verification, we are inclined to believe in the existence of clays showing a diffraction peak at 15.0 Å or 15.3 Å.

It may be most plausible to consider that each small individual diffraction peak scattered was produced by either of (001) reflection of some kind of mineral and or (002), (003) reflections from the clays with high basal spacings. However, in the case of the prominent peaks, they will be resulted from the high amount of the clays and the integral of diffractions given by both of the above mentioned.

An occurrence of numerous varieties of mixed-layer minerals having large basal spacings is the principal reason to complicate the X-ray diffraction figures in the high intensity portion of a relatively low angle and the reason to produce scattered or diffused-like diffractions of numerous small peaks in the regions of a relatively high angle such as from 9.0 to 4.5 Å and from 4.0 Å to 2.0 Å.

### Discussion

It may not be so incorrect to consider that the soil condition in paddy soils are quite different in some points from that of well-drained upland soils because very favorable conditions for a formation of clays prevail during several months of paddy-planting period in the summer, especially, under very strongly reduced conditions of low redox potentials. However, paddy soils are laid down under a relatively well-drained condition from October to the next late spring. Such severe fluctuation during one year between strong reduction and high oxidation would provide the soil conditions a particular position in the soil forming process, especially, in the type of clays formed. Consequently, clays formed by the alteration of the original minerals and those newly formed would become a particular type. We have already reported on clay minerals in a calcareous alkaline paddy soil. In the present paper we clarified the clays in a paddy soil with acid reaction such as pH 4.9.

According to the results of our investigations, the finest clay fractions here studied,  $<0.15\mu$ , are quite similar to that in an alkaline paddy soils from the view point of differential thermal analysis curves and X-ray diffraction powder patterns, although they differ somewhat in chemical compositions. The former possesses a molar ratio of  $\text{SiO}_2/\text{R}_2\text{O}_3$  of 2.28 but the latter had a ratio of 3.0. The differences in the chemical compositions and the discrepancy in the  $\text{SiO}_2/\text{R}_2\text{O}_3$  molar ratios seem to be due to the degree of isomorphous substitution,

especially, the latter must be a result from Al-substitution for Si-atoms in the tetrahedral layers. Notwithstanding such a difference, it must be noticed that the kinds and forms of crystal lattice structure can remain quite the same. An idea which has generally been accepted that principal clay minerals formed in paddy soils are halloysite, kaolinite or 1:1 layer lattice type clay minerals should be discarded. Because clays having such a low molar ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  as 2.0 or slightly higher contains no or only a very small amount, if any, of halloysite but consisting mainly of the mixed-layer or stratified minerals which possesses relatively strong expanding characters and high cation exchange capacity regardless of soil reaction. Furthermore, it must be noticed that particles of larger diameter such as medium silt of 9–11 $\mu$  are almost alike the finest clay of <0.15 $\mu$  and indications of illite and halloysite, through X-ray investigation, could hardly be recognized. That the similarity of the X-ray diffraction can be seen over a very wide range of particle sizes such as from <0.15 $\mu$  to 9–11 $\mu$  are an important fact because if clay minerals are formed by destruction or alteration of large particles in the direction of finer ones it is very surprising that such large particles as 10 $\mu$  have already been altered to a structure which is quite similar to those finer than 0.15 $\mu$  and if the large particles as 10 $\mu$  developed as a result of growth from fine particle as <0.15 $\mu$  it should also be a surprising phenomenon.

On all of the X-ray diffraction diagrams of the clays here studied, there can be seen numerous small peaks of diffractions in a somewhat scattered form, particularly, in the region of a relatively low angle such as from 5 Å to 9.5 Å or from 2 Å to 4 Å. Regarding the X-ray scattering in a region of small angle by colloid, clay minerals, or stratified minerals several interpretations or discussions have been offered by workers as J. Mering(13), Brindley(14), Porod(15), McEvan(12), and others. Measuring a scattering of X-ray as the parameters of thickness and structure of the stratified layers, their relative abundance, and their degree of disorder, Brindley interpreted a scattering of broadened reflection to lattice mistakes, smallness of particle size and the 3-dimensional character of diffraction. Porod emphasized the effect of interparticular interferences, especially when clays are large leaf-shaped micelles. McEvan and Grim(16) illustrated as a result of the combination of two different clays giving different basal spacings according to scattering intensity factor formula. The scattered small diffraction peaks or broad band-like reflections with a high intensity which appeared on our diffraction diagrams can not be interpreted by any of the explanations just mentioned. From a series of small peaks successively arranged it is reasonable to consider that there exist different minerals corresponding to all or most of the observable diffraction peaks. Such numerous varieties of diffraction peaks may be formed not only through the magnitude of particle size and disorder in lattice structure but mainly through the differences in thickness

or forms of packing layers, in other words, by complexity of the kinds of lattice layers.

The principal reason for the occurrence of such numerous varieties of layer minerals differing only slightly in their X-ray diffraction peaks can be attributed to the particular conditions of the paddy soils. With regard to the formation of the clay minerals having large basal spacings, Jackson (11) Brindley (17) Nagelschmidt (18) and others have reported. All of these workers interpreted the interstratification of clay minerals as such two lattice layers with different basal spacings to be due to the contraction by actions of cations as such as potassium atoms. On the contrary, Sudo (19) explained the occurrence of the mixed-layer clays showing diffraction at 11.7, 14.7, and 29.8 kX, to have been formed as the result of contraction of montmorillonite layers interleaved by a gibbsite-like layer of Al-atoms. The clays show diffraction at 23.6 kX when their adsorbed water were removed completely and at 32-33 kX when saturated with water. The clay samples which Sudo used were obtained from the Kurata Mine, Yamaguchi Prefecture, where the origin is considered to be a geological formation.

On the diagrams of X-ray diffraction micrographs of our clays we can recognize diffraction peaks which correspond to those given by Sudo. Although the origin of Sudo's clays is a geological process, the same mixed-layer clays may probably be formed under conditions of paddy soils provided there is a sufficient supply of active or soluble Al-ions and a very poor supply of mono- and divalent cations such as in a strongly acid environment. An interstratification by Al-layer is a very beneficial concept to explain the low silica : alumina molar ratio and the small contents of MgO, K<sub>2</sub>O, and CaO in the clays here studied. In addition, if contraction of mixed layers of clays is constructed mainly by Al-atoms in sheets between 2 : 1 lattice layers, there would be produced OH-groups which are more similar to OH-groups in halloysite rather than gibbsite. This can be considered as an important reason when considering the differential thermal curves of our clays which are quite similar in the range from 400° to 600°C to that of halloysite excepting that the peak temperature of the former is lower about 30°C or 40°C than the latter. Especially, that the shape of the differential thermal curves between 400° and 450°C is quite the same as that of halloysite, regardless of the absence of halloysite, will support the existence of such interleaved Al-layers in stratifications. Recently, Robertson discussed the influences of disorder in crystal structure on an endothermic peak temperature. It is generally accepted that many clays formed or present in soils show endothermic peak temperature at or near 530°C or 540°C. Such a low temperature of endothermic peak can occur, of course, from disorder in crystal lattice or in packing of lattice layers, however, in the case of the clays having a low content of K<sub>2</sub>O and a low SiO<sub>2</sub>/R<sub>2</sub>O<sub>3</sub> ratio, OH-groups connected to interleaved Al-atoms may be acting an important role. If stratification of the mixed-layer minerals of not only



those which are contracted by K-atoms between layers of montmorillonite, vermiculite, hydrobiotite and illite but also those which are contracted through Al-layers arranged in sheets are possible to be formed, it may not be incorrect to propose an assumption that on the outermost surfaces of 2:1 layer lattice mineral particles Al-atoms are arranged in a sheet and onto these Al-layers Si-ions can be arranged, as if in sheet, attracted from soil solution in such a way that the halloysite cell is contracted on the outermost surface of one or both sides of a layer lattice mineral. By a combined effect of interstratification which has been already proposed including a contraction by Al-layer and contraction of halloysite-like 1:1 layer lattice on the outermost surface plane of interstratified minerals we can, without difficulty, explain the diffraction peaks over 20.0 Å as actual reflections from the basal planes of the real stratified mixed-layer minerals. The clays of large particle size which contain potassium to a considerable extent can be considered to consist of minerals formed by contraction of K atoms, accordingly, they must contain illite- or mica-layer in their forms of stratification. Gruner has asked on a point that why interstratification of different silicate layers do not occur more frequently than hitherto was found and he suggested that the relatively stationary or only slowly changing chemical environment may act rather than in any aversion of different types of layers to one another. The conditions considered by Gruner may well correspond to the conditions of ordinary natural soils, however, the conditions in paddy soils may differ distinctly from those of natural well-drained upland soils in the points that there prevail very severe and abrupt fluctuations of environments such as from stagnant to well-drained, from strong reduced conditions to oxidative, from element supplying by irrigation to element lossing by leaching. Several months will be most favorable for the condition of new synthesis of clay minerals during which, however, conditions probably vary and fluctuate to a considerable extent. Such conditions in paddy soils would produce far much more kinds of clay minerals than usually expected or than that supposed by Gruner. Considering from the fact that X-ray diffraction peaks of the clays having very large particle sizes such as  $2.0\mu$  or more showing very similar features or differ only slightly, if any, compared with those of the clays finer than  $0.15\mu$  it may probably be possible to consider that the clays of large particle size are formed through growth step by step from finer particles in which Al atoms may play an important role. However, it must be kept in mind that there may be a possibility of a clay formation by the alteration of primary minerals toward smaller particle sizes according to the process of "preferential weathering" of mica-layer proposed by Jackson. From the present state of our knowledge, we are unable to explain either of these interpretations for clay forming process is actually proceeding in paddy soils. As a conclusion, however, we may state that more or less particular conditions

of paddy soils can help or accelerate a formation of such numerous kinds of varied clay minerals.

### Summary

A clay portion ( $<2.0\mu$ ) separated from a surface layer of an acid paddy soil (pH 4.90) was fractionated into four fractions  $<0.15\mu$ ,  $<0.6\mu$ ,  $0.6-1.0\mu$  and  $1.0-2.0\mu$ , according to particle size, and after being converted into H-clays they have been investigated by chemical analysis, differential thermal analysis, and X-ray diffraction spectrometer.

All fractions, regardless of their particle sizes, consist mainly of large amounts of expanding 2 : 1 layer lattice minerals and of stratified mixed-layer minerals giving large basal spacings accompanied by small portions of halloysite (in the fractions larger than  $0.15\mu$ ) and some quartz and cristobalite (in the fractions larger than  $0.6\mu$ ).

The silica : alumina ratio and silica : sesquioxide ratios are very low (about 2.30) and the contents of  $\text{Fe}_2\text{O}_3$  (including FeO) are relatively low (about 8 per cent). The contents of MgO and CaO are very minute (former is  $<1.0$  per cent, the latter is  $<0.1$  per cent). The content of  $\text{K}_2\text{O}$  is only 0.35 per cent in the clays  $<0.15\mu$  but that of the clays of larger particle size amounts to 2.5-4.0 per cent.

The differential thermal curves of all fractions except that of  $<0.15\mu$  are quite similar and large sharp-endothermic peaks occur at  $140^\circ\text{C}$  and  $530^\circ$  or  $540^\circ\text{C}$  but relatively small and broad exothermic peaks at  $900^\circ$  or  $920^\circ\text{C}$ .

On X-ray diffraction micrographs no distinct diffraction line of  $10 \text{ \AA}$  can be observed although small reflections of halloysite appeared at 7.2 or 7.4  $\text{\AA}$ .

The authors conclude that the principal clay minerals other than small amounts of halloysite, quartz and cristobalite would be some expanding 2 : 1 lattice clay and stratified mixed-layer minerals having very numerous, different, large basal spacings which are formed mainly by the contraction with Al-layer, probably gibbsite-like layer, and layers of 2 : 1 layer type minerals of montmorillonite groups and/or illite, and that those clays may be a result of the new formation under particular conditions which prevail in paddy soils.

### Acknowledgement

The writers thank Professor Sakae, Takeuchi and Mr. Kazuo, Furukawa (Research Institute for Iron Steel and other Metals, Tohoku University) who kindly assisted in the investigations of the clay samples using the X-ray diffraction spectrometer.

**References**

- 1) Uchiyama, N. and Onikura, Y. (1954). *J. Sci. Soil and Manure* **24**, 271, 307.
- 2) Barshad, I. (1954). *Soil Sci.* **78**, 57.
- 3) Uchiyama, N. and Onikura, Y. (1954). in press.
- 4) Robertson, R. H. S. (1954). *Amer. Min.* **39**, 118.
- 5) Grimshaw, R. W., Heaton, E., and Roberts, A. L. (1945). *Trans. Ceramic Soc. (Eng.)* **44**, 76.
- 6) Sand, L. B. and Bates, T. E. (1953). *Amer. Min.* **38**, 291.
- 7) Grimshaw, R. W., Heaton, E., and Roberts, A. L. (1945). *Trans. Brit. Cer. Soc.* **44**, 69.
- 8) Gruner, J. W. (1948). *Amer. Min.* **33**, 698.
- 9) Bramao, L., Cady, J. G., Hendricks, S. B., and Swerdlow, M. (1952). *Soil Sci.* **73**, 273.
- 10) Murray, H. H. (1954). *Amer. Min.* **39**, 97.
- 11) Jackson, M. L. et. al. (1952). *Soil Sci. Soc. Amer. Proc.* **16**, 3.
- 12) McEvan, D. M. C. (1949). *J. Soil Sci.* **1**, 90.
- 13) Mering, J. (1950). *Trans. 4th Int. Cong. Soil Sci. Amsterdam* **3**, 21.
- 14) Brindley, G. W. and Robinson, K. (1946). *Trans. Faraday Soc.* **42 B** 198.
- 15) Porod, I. G. (1951). *Kolloid Zt.* **124**, 83.
- 16) Grim, R. E. (1953). *Clay Mineralogy.*
- 17) Brindley, G. W. (1951). *Discussion Faraday Soc.* **11**, 75.
- 18) Nagelschmidt, N. (1944). *Min. Mag.* **27**, 59.
- 19) Sudo, T. et. al. (1954). *Jap. J. Geol. Geogr.* **24**, 71.