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著者	UCHIYAMA Nobuo, ONIKURA Yutaka
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DOUBLE-LAYER MICA MINERALS IN PADDY SOIL

By

Nobuo UCHIYAMA and Yutaka ONIKURA

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

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Introduction

Caillère(1), Mathieu-Sicaud and Henin(2), reported on mica-type minerals having layers of water molecules separating double-mica-like minerals. This was named "Allewardite" according to a locality near Alleward, France. Recently, Brindley(3) has reported on these minerals in detrit. According to him, these minerals gave a long series of basal reflections such as 28.36 Å when immersed in water, 24.62 Å in air-dried condition, and 19.09 Å when heated at 450°C. The aluminosilicate layers have been shown to be essentially the same as in the muscovite structure. Henin, Esquevin and Caillère(4) assumed a structural formula of this mineral as consisting from 12 ions of Si, Al, Fe, and Mg in tetrahedral and octahedral positions, as in muscovite. The minerals are considered to be characteristic in the facts that they possess a relatively low content of K₂O and a very high amount of H₂O⁺ as high as 6.04 per cent.

It may be reasonable to consider that these minerals are not necessarily rare in soils because they would be naturally formed as a result of weathering of muscovite. We must here recall the assumption proposed by Jackson (6) as "Preferential weathering" theory in which he interpreted the form of weathering of mica to proceed on alternately layers much more strongly. If such a form of weathering proceeds to an extreme degree we can suppose a type of mica layer where two units of mica-structure are contracted relatively tight through cation atoms, mainly K-atoms not exchanged, but the outside of these two linked units are freed from other units and opened against water or a solution of environment. Recently, we have found clay minerals quite similar to allewardite in a paddy soil in Iwanuma Town, Miyagi Prefecture.

Preparation of Samples and Experimental Procedures

The soil from which the clays were separated is an alluvial deposit transported by the Abukuma River. The clay fraction (<2.0 μ) was separated from a soil of surface-cultivated layer having a depth of 15 cm. by sedimentation after being freed from organic matter. The suspension containing the

clay fractions was centrifuged to sediment a fraction having particle diameter larger than 1.0μ , then, a suspension containing clay fractions smaller than 1.0μ was centrifuged to separate a portion containing those larger than 0.6μ . Thus, the separated two portions of $0.6\sim 1.0\mu$ and $1.0\sim 2.0\mu$ were purified by centrifuging for several times to free them from particles of larger or smaller than the required size limits, respectively. Thus the prepared two clay fractions were treated with the reduction method using nascent hydrogen and then with 2 per cent Na_2CO_3 solution to free them from SiO_2 -gels and hydrous oxide gels of Al_2O_3 and Fe_2O_3 . After the clays were converted to Na-clays by N-NaCl solution and equilibrated against 50 per cent R. H. in a desiccator we examined them by chemical analysis, D. T. A. and X-ray diffraction method.

Results of Chemical Analysis

Two fractions of Na-clay have been analyzed chemically. The results are shown in the first column in Table 1. The chemical constituents of the original samples are characteristic in that the contents of H_2O^+ are relatively high and C. E. C. are more or less high even when colloidal clay fractions smaller than 0.6μ are excluded, in addition, the content of K_2O is fairly low. As later been clarified by X-ray diffraction results, these clays contain considerable amounts of quartz + cristobalite and kaolinite.

Table 1. Chemical Analysis of Two Clay Fractions separated from a Paddy Soil and Alleverdite

	Fine clay			Coarse clay			Alleverdite
	original sample	calculated on A-basis	B-basis	original sample	calculated on A-basis	B-basis	
SiO_2	55.84	49.81	51.37	62.77	49.69	51.19	50.06
Al_2O_3	25.57	29.05	24.10	21.49	29.04	24.07	35.51
Fe_2O_3	6.68	7.59	11.16	5.60	7.56	11.12	0.99
MgO	1.21	1.37	2.01	1.00	1.35	1.99	0.39
CaO	0.25	0.28	0.42	0.37	0.50	0.73	1.17
K_2O	1.01	1.14	1.68	1.12	1.51	2.22	1.22
Na_2O	1.51	1.72	2.52	1.08	1.46	2.15	2.49
H_2O^+	7.88	8.95	6.57	6.47	8.74	6.26	6.66
C. E. C. me.	48.7	55.4	74.4	34.4	46.6	61.5	—

A-basis contents on quartz (+cristobalite) free basis

B-basis contents on the basis freed from quartz and kaolinite

To find out the chemical compositions or structural formulas of the principal clay minerals in a nearly pure state, it is necessary to eliminate the quantities of subordinate clays such as quartz and kaolinite. It is very difficult to determine the precise contents of quartz + cristobalite and kaolinite, but, when we calculate them by measurements of X-ray diffraction intensities, the obtained values would not be so far from the correct contents. The calculated contents of the sum of quartz and cristobalite according to the intensities of

diffractions at 4.21 Å and 3.35 Å for quartz, and 4.05 Å and 3.21 Å for cristobalite became 12 per cent (0.6~1.0 μ) and 26 per cent (1.0~2.0 μ), respectively. The contents of kaolinite measured through X-ray diffraction intensities at 7.14 Å were both 32 per cent of quartz-freed clays, accordingly, they correspond to 28.16 per cent (0.6~1.0 μ) and 23.68 per cent (1.0~2.0 μ) in the cases of the original clays. Consequently, the assumed principal clays in nearly pure state would be about 59.84 per cent (0.6~1.0 μ) and 50.32 per cent (1.0~2.0 μ) of the original clays.

When these values are nearly correct and the very small amounts of other accessory minerals are neglected, the chemical compositions of the principal clays may be as those shown on the (B)-basis column in Table 1. If we discuss the chemical compositions of the principal clays indicated in (B)-basis column as the correct one, they resemble that of allevardite reported by Henin, Esquevin, and Caillère(4). However, they differ in some points from allevardite, to say, the amounts of Fe₂O₃ is very high and MgO is also considerably high, on the contrary, Al₂O₃ is more or less small. In addition, the amounts of Al-substitution in a tetrahedral layer are somewhat low. The water contents are considerably high in the original samples but they become 6.57 per cent (0.6~1.0 μ) and 6.26 per cent (1.0~2.0 μ) and are nearly equal to that of allevardite. The values of C. E. C. of the original clays are 48.7 me. (0.6~1.0 μ) and 33.4 me. (1.0~2.0 μ) per 100 g clays, however, they become fairly high after calculations such as 74.4 and 61.5 me., respectively. If these calculations are reasonably accepted, such high values of C. E. C. are impossible to attribute to illites or 1:1 lattice-type minerals, then, we consider it is most plausible that they are 2:1 lattice-type minerals which contain 1.68 and 2.22 per cent of K₂O.

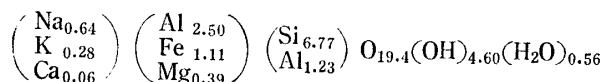
As explained later, there is no X-ray diffraction indicating an existence of montmorillonite group minerals and illites, for example, we can not observe any diffractions at 15.0, 7.50, 10.0, 5.0, and 3.33 Å.

According to the results of preliminary chemical analysis of H-clays the contents of Na₂O were only a trace, therefore, they would contain Na₂O in only negligible amounts, then, we determined the contents of Na₂O of Na-clays by calculation from their C. E. C. The structural formulas of these clays constructed from the chemical constituents in (B)-basis column as assuming on a pure state are shown in Table 2 where that of allevardite modified by Brindley (3) is also indicated for comparison.

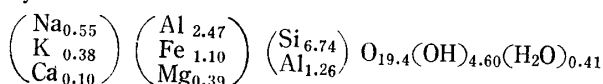
It can be seen from Table 2 that both of our clays and that of allevardite are quite similar. Although allevardite has Al-substitution of 1.60 in a tetrahedral layer, the clays here studied have more or less small amounts such as 1.23 and 1.26. This may be induced by the presence of accessory minerals in small amounts, however, we can suppose another reason such that there would be conditions to decrease Al-tetrahedrons by the breaking actions of environments

Table 2. Structural Formulas of Two Clay Fractions from Paddy Soil and Allevardite

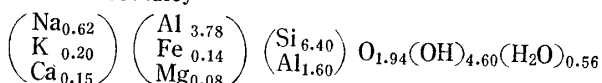
Fine clay



Coarse clay



Allevardite after Brindley



or by weakness owing to unbalancity in crystal structures resulting in the decreases of their Al-tetrahedrons. If this is the case, there may be certain conditions by which the amounts of Al-substitution could be increased. The experimental proof which concern to the problem is reported in other article (5). That the contents of Fe_2O_3 are very high as such as 11.1 per cent on a pure clays basis should be attributed to a condition of stagnated paddy soils where highly active Fe^{2+} ions are predominant. The amounts of interlayer water molecules in the case of finer clays is just equal to allevardite but the coarser clays contain slightly less amounts.

Differential Thermal Analysis

D. T. A. curves of two clay fractions heated at a rate of 10°C per min. are shown in Fig. 1. The first endothermic peak occurs at 155°C and the second at 545°C and 550°C . The exothermic peak appears at 900°C ($0.6\sim 1.0\mu$) and 910°C ($1.0\sim 2.0\mu$). There is no indications of the presence of other minerals as those of montmorillonites, illites, and chlorites in a recognizable amount. The shape

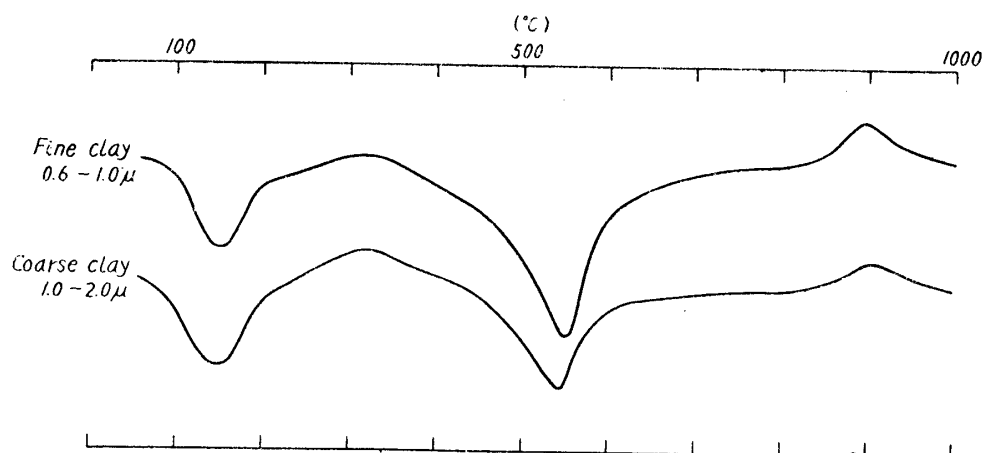


Fig. 1. D. T. A. curves of two clay fractions separated from a paddy soil.

of the second endothermic peak rather resembles illites though its peak temperature is far below. Accordingly, we consider that the principal clay portion may be clays having a crystal structure of illitic nature but in the same time possessing high capacity to adsorb water on their surface planes.

X-ray Diffraction Analysis

Two grain size fractions of Na-clays equilibrated against 50 per cent R. H. have been examined on exposure to $\text{Cu-K}\alpha_1$ radiation and recorded by an automatic Geiger counting micrometer. The results are shown in Fig. 2.

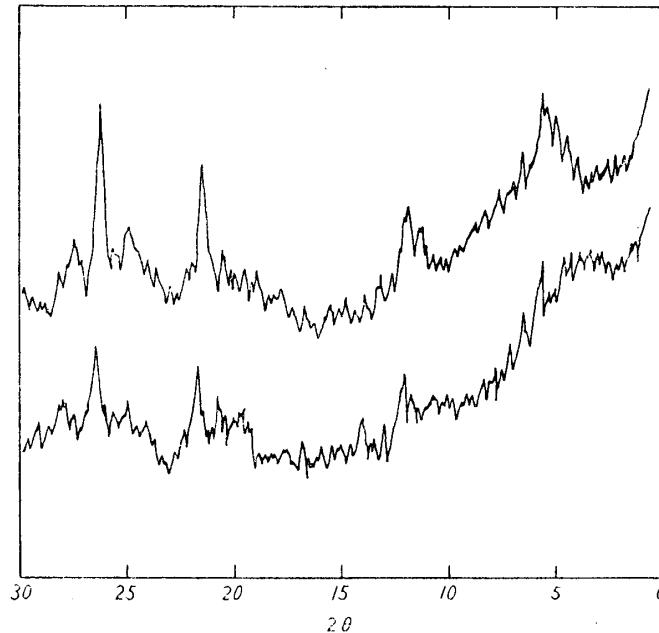


Fig. 2. X-ray diffraction micrograms of Na-clays of two grain size fractions ($0.6\sim 1.0\mu$ and $1.0\sim 2.0\mu$) separated from a paddy soil in the angle region smaller than $2\theta = 30^\circ$
 upper; $1.0\sim 2.0\mu$ fraction
 lower; $0.6\sim 1.0\mu$ fraction.

The prominent diffraction peaks at $4.05, 3.35 \text{ \AA}$ and relatively less intense peaks at 4.21 and 3.21 \AA are observed. These are considered to be indications of quartz and cristobalite or amorphous silica. The diffractions at 7.14 and 3.57 \AA are fairly intense and also we can observe clear diffraction at 1.483 \AA . These are considered to be attributed to kaolinite. The most intense diffraction in the low angle region is observed at 14.30 \AA with a nature of broad-band type. Two less intense and small peaks appear at 12.32 and 11.04 \AA . As is seen in Fig. 2, although we can not recognize highly intense reflections larger than 14.3 \AA , we consider that these three reflections of $14.3, 12.32,$ and 11.04 \AA

would be (002) of long spacing series of 28.6, 24.64 and 22.08 Å. If these are so, they nearly correspond to 28.4, 24.64 and 22.00 Å of allevardite having three, two and one layers of interlayer water, respectively.

When diffractions were examined after heating at 600°C for 8 hours, the reflection at 9.75 Å became far more intense. If this is a reflection of (002) of our double-layer mica minerals having none of water layers, this is 19.50 Å and slightly larger than 19.28 ± 0.04 Å of allevardite. Therefore, we consider that (001) of these clays should be 28.60 Å.

$$19.50 + 9.08 = 28.58$$

$$19.28 + 9.08 = 28.36$$

An expanding of c_0 -plane is considered to be induced by large numbers of Fe-atoms and Mg-atoms in an octahedral layer.

It must be noticed that indications of X-ray diffraction showing trioctalayer minerals such as 4.70~4.80 Å and 1.58~1.65 Å are hardly observed. This may be a convincing proof that these clays contain no or negligible amount of trioctalayer but a principal portion of them would be a dioctahedral type of minerals, because diffractions at 1.499~1.503 Å are clearly observed.

Discussion

As a weathering of muscovite proceeds cations, mainly K-atoms fixed between two mica units, are lost, and accordingly, a vacant area where K-atoms had been fixed before is formed. Although unbalance between lengths of tetra- and octalayer are protected when K-atoms are fixed, as soon as K-atoms are lost unbalance or weakness of structure takes place then it is exposed to the attacks of environmental forces. Especially, when weathering goes on more stronger on alternate layers the surface planes of the more weathered side will gradually show more unbalance or become more weaker than the sides of the Si-tetralayer facing to the sides where more K atoms remain. To prevent clay structure from destruction of the tetralayers against weathering forces, in other words, to prevent the tendency to decrease Al-tetrahedrons from the tetralayer it is necessary that some octahedrons such as Mg^{2+} or Fe^{2+} should be added to an octalayer for elongation of the octahedral layer. This may be the reason for the linear relationship existing between the contents of MgO and K_2O in illites or illitic minerals. Al-tetrahedrons protected by the balancing action resulted from the increasing of octahedrons will possess negative charges. Negative charges on the surface of a Si-tetrahedral layer facing water or the solution of an environment are balanced or neutralized by exchangeable cations from the solution. However, those on the Si-tetrahedral surfaces contracted more or less tightly through the fixed non-exchangeable cations can not be balanced by the exchangeable cations from the

solution owing to the narrowness of the interlayer width. Then, the water molecules can enter into the interlayer position in a thickness of only one layer of water molecules. If this is so, between negative charges of Al-tetrahedrons exposed on both two units of mica structures and one molecule of water newly penetrated from the outer solution there would be produced a hydrogen-bond linkages. This may be the reason that interlayer water molecules in an unit of doublelayer mica minerals are not lost at a temperature till as high as 240°C.

If this is the case, we can consider some relationship between the amounts of Al-substitution in a tetralayer, especially when they are newly formed or increased by certain conditions, and the amounts of interlayer water molecules. The finer clay fraction here studied possess 0.56 mols of interlayer water which just equals to that of allevardite, but in the case of coarser clay fraction it is slightly smaller, 0.41 mols.

Al-substitutions are more or less small in amount than allevardite such as 1.23 and 1.26. We consider that such a low Al-substitution should be attributed to the more intense weathering action of the paddy fields and/or to a deficiency of Mg-ions to enter in an octalayer compared with the strength of attacking actions operating onto Al-tetrahedrons in Si-tetralayers, in other words, the entering of Mg-ions as a form of an octahedron is very slow but the Al-tetrahedron is attacked rapidly, consequently, the interlayer water molecules become far lesser fixed.

Summary

Two grain size portions of clays ($0.6\sim 1.0\mu$ and $1.0\sim 2.0\mu$) separated from a surface layer of a paddy soil are discussed according to the results of chemical analysis, D. T. A. and X-ray diffraction analysis. Both of these two clay portions are quite the same. The contents of K_2O are very low but Fe_2O_3 and MgO are relatively high. They contain fairly large amounts of loss on ignition above 240°C and it is interpreted as interlayer water. From X-ray diffractions, we defined them as swelling double-layer mica minerals resembling allevardite.

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