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REACTION BETWEEN Mg-IONS AND DOUBLE-LAYER MICA-MINERALS

By

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Usually, illites, illitic minerals or mica-minerals contain a considerable amount of MgO, in some clays they are relatively low but in others as high as 7 per cent. In general, the amounts of MgO show a tendency to be large when the contents of K₂O are small, the relationship has been discussed by the senior author (1). We have experienced in 1954 such a phenomenon that when a paddy soil containing double-layer mica minerals was laid under a stagnant condition for a year the clays separated from the soil at the end of stagnation increased their MgO content slightly and decreased C. E. C. to some extent. The amount of MgO increased by 0.23 per cent, that from 0.83 per cent to 1.06 per cent, and the amount of C. E. C. dropped by 66 me. per 100 g clays from 74.8 me. to 68.2 me. In this case, the reduction of C. E. C. per 1 g of MgO increased corresponds to as high as 28.7 me. per 100 g clays. We considered the reason of such a phenomenon that the Mg-ions in the soil solution entered into a octahedral layer and the amount of positive charges corresponding to increased Mg-atoms might balanced the negative charges in the clays. If this is the case, clays having more illitic characters, to say, clay portions of larger particle diameter, for example, 0.6~1.0 μ and 1.0~2.0 μ , will show much more pronounced reaction with Mg-ions. To detect this point, we experimented on the reaction of coarse clay fractions separated from the same paddy soil above mentioned with N-MgCl₂ solution.

Samples used and Experimental Procedures

Clay samples used in this study are swelling double-layer mica minerals which are quite similar to allevardite reported by Brindley(2). According to X-ray diffraction investigations, they show basal reflections of 28.6, 24.6 and 14.3, 12.3 Å and small reflection of 11.0 Å when equilibrated to 50 per cent R. H. The contents of MgO and K₂O are 1.0~1.2 and 1~1.1 per cent, respectively. They contain a relatively high amount of water such as 6.74 (1.0~2.0 μ) and 7.88 per cent (0.6~1.0 μ) over 240°C. Some portion of these water is considered

to be present as an interlayer water between two units of mica structure. The cation exchange capacities are as high as 34.4 me. ($1.0\sim 2.0\mu$) and 48.7 me. ($0.6\sim 1.0\mu$) even though they contain considerable amounts of quartz and kaolinite. These clays of two grain size fractions of $0.6\sim 1.0\mu$ and $1.0\sim 2.0\mu$ were separated by centrifuge and sedimentary methods from a paddy soil which is the same as that used in the studies already reported(1). The clays of two fractions were purified according to a given grain size by centrifuging several times. At first organic matter was destructed by 6 per cent H_2O_2 , and then freed from Fe_2O_3 hydrous oxide by the reduction method, then from the free SiO_2 - and Al_2O_3 -gels by boiling with 2 per cent Na_2CO_3 solution. After these treatments the clays were converted into Na-clays by leaching with N-NaCl solution and then washed, dried, pulverized, and equilibrated against 50 per cent R.H. in a desiccator. Two grams portions of the purified samples were boiled with 600 c.c. of N- $MgCl_2$ solution for three days, eight hours every day. Mg-treated samples were filtered, washed and leached with N-NaCl solution to exchange all the adsorbed exchangeable Mg-ions, then washed with ethyl alcohol, dried, pulverized, and equilibrated to 50 per cent R.H. Each two non-treated and Mg-treated samples of two grain size fractions of $0.6\sim 1.0\mu$ and $1.0\sim 2.0\mu$ were analyzed chemically according to the usual method, by D. T. A. method at a heating rate of $10^\circ C$ per min., and by X-ray diffractin method using the automatic Geiger counting micrograph on exposure to $Cu-K_{\alpha_1}$ radiation. Experimental results of non-treated clays have been reported and discussed in detail in an other article (3).

Variations of Chemical Constituents by Mg-treatment

The results of chemical analysis after treating with $MgCl_2$ solution and, for comparison, that of non-treated clays are shown on the columns of "original sample" in Table 1. As can be seen from Table 1, considerable variations of some constituents occurred. The contents of SiO_2 , Na_2O , and C. E. C. decreased, however, the amounts of MgO and H_2O^+ (over $240^\circ C$) increased according to the values of the original samples. The contents of Al_2O_3 and K_2O remained nearly unaltered though some of them appeared as if slightly decreased. In this case, the amounts of Na_2O were determined by calculation which just correspond to the value of their cation exchange capacity. We can say that almost all of Na_2O are exchangeable and the Na_2O fixed in non-exchangeable form may be negligible because the adding of exchangeable Na_2O exceed only a little over 100 per cent and in other experiments of the same H-clays contain only trace of Na_2O . The amounts of Na_2O decreased by Mg-treatment are considered to be due to the reduction of C. E. C. An increase of MgO contents is the result of reaction of clays with $MgCl_2$ solution. Also, an increase of H_2O^+ (over $240^\circ C$) may be considered to be due

Table 1. Chemical Constituents of Two Clay Fractions before and after treatment with MgCl₂ Solution

(I) Fine clay fraction (0.6~1.0 μ)

	before treatment			after treated with MgCl ₂			
	original sample	calculated on A-basis	calculated on B-basis	original sample	calculated on A-basis	calculated on B-basis	calculated on C-basis
SiO ₂	55.84	49.81	51.37	53.96	47.68	48.24	49.85
Al ₂ O ₃	25.57	29.05	24.10	25.05	28.46	23.22	24.00
Fe ₂ O ₃	6.68	7.59	11.16	6.53	7.42	10.91	11.15
MgO	1.21	1.37	2.01	2.81	3.19	4.69	2.55
CaO	0.25	0.28	0.42	0.72	0.82	1.21	1.25
K ₂ O	1.01	1.14	1.68	0.96	1.09	1.60	1.65
Na ₂ O	1.51	1.72	2.52	0.96	1.09	1.60	1.65
•H ₂ O ⁺	7.88	8.95	6.57	9.06	10.30	8.56	7.81
C. E. C. me.	48.7	55.4	74.4*	31.0	35.3	44.9*	46.4

(II) Coarse clay fraction (1.0~2.0 μ)

SiO ₂	62.77	49.69	51.19	61.16	47.51	47.98	49.54
Al ₂ O ₃	21.49	29.04	24.07	20.95	28.31	23.00	23.75
Fe ₂ O ₃	5.60	7.56	11.12	5.43	7.34	10.79	11.14
MgO	1.00	1.35	1.99	2.35	3.17	4.67	2.57
CaO	0.37	0.50	0.73	0.61	0.82	1.20	1.25
K ₂ O	1.12	1.51	2.22	1.09	1.47	2.16	2.23
Na ₂ O	1.08	1.46	2.15	0.62	0.84	1.05	1.08
•H ₂ O ⁺	6.47	8.74	6.26	7.47	10.10	8.27	7.53
C. E. C. me.	34.4	46.6	61.5*	20.0	27.0	32.7*	33.7

• loss of weight when heated over 240°C.

* C. E. C. of kaolinite is assumed to be 15 me./100 g.

A-basis freed from quartz, quartz contents are 12% (0.6~1.0 μ) and 26% (1.0~2.0 μ).

B-basis freed from quartz and kaolinite, kaolinite contents are 28.16% (0.6~1.0 μ) and 23.68% (1.0~2.0 μ).

C-basis freed from brucite contents in B-basis values, contents of brucite are 2.23 MgO, 1.00 H₂O (0.6~1.0 μ) and 2.16% MgO, 0.96% H₂O (1.0~2.0 μ).

to an increase of interlayer water between two mica-units. The fact that the contents of Al₂O₃, Fe₂O₃ and K₂O remained almost unaltered shows that almost no influence has been given by Mg-ions on these three elements in lattice structure. The amounts of C. E. C. decreased by Mg-treatment are 17.4 me. (0.6~1.0 μ) and 14.4 me. (1.0~2.0 μ) and if we calculate C. E. C. reduction per 1 g of MgO increased, they are 10.9 me. in the former and 10.7 me. in the latter. Here, we must be aware of the fact that the clays contain considerable amounts of impurity minerals such as quartz or kaolinite, and thus, the variations which appear may not indicate the true alterations of the constituents. Therefore, we feel that certain calculations are necessary to discuss the variations of principal clays on a pure state basis. Fortunately, we have already determined them and reported(3) on the compositions of clays in the samples. According to the results, there are somewhat high amounts of quartz and cristobalite and kaolinite, and very small amounts not larger than several per cent of trioctahedral minerals such as hydrobiotite and/or vermiculitic clays.

However, the principal portions, probably nearly equal to or larger than one half of the whole, are swelling double-layer diocta-mica minerals similar to allevardite which had been reported by Brindly(2). The amounts of accessory minerals determined are as follows :

Fraction of samples	Quartz + Cristobalite	Kaolinite
0.6~1.0 μ	12 %	28.16 %
1.0~2.0 μ	26 "	23.68 "

When we assumed that after Mg-treatment there occurred no alteration of quartz and kaolinite and that when some variations appeared they are changes of principal clays of dioctalayer and of triocta-minerals as an accessory, the same calculation can be applied both before and after treatment with $MgCl_2$ except for the calculation of changes induced by Mg-ions.

For the changes by Mg-ions we make an assumption as follows. When reductions of C. E. C. have occurred by Mg-treatments the possible reactions to be considered may be those of the following three cases.

- 1) destruction of some clays having C. E. C.
- 2) alteration of clay structure toward lowering of C. E. C. such as increasing of Mg-octahedron in an octahedral layer.
- 3) closing up of charged surface of clays by Mg-ions such as chlorites formation by brucite layer.

If the variations of (2) and (3) occurred to some extent they could be detected through D. T. A. curves or X-ray diffraction figures, and, as be explained in later, we could observe them. From the results of examinations by D. T. A. and X-ray diffractions we arrived to the conclusion that the second and the third cases of the above mentioned would be the principal reasons for the reduction of their C. E. C.

When chlorites are formed by Mg-ions the reduction of C. E. C. should be about 3.1 me. per 1 g MgO increased per 100 g clays provided C. E. C. of the clays is 100 me. per 100 g of clays. On the contrary, a reduction of C. E. C. induced by an increase of Mg-octahedron in a diocta-layer would be about 49.5 me. per 1 g of MgO increased.

Here, being the reductions of C. E. C. of these clays 17.4 and 14.4 me., we assumed that the reduction of C. E. C. would be induced by both of the low values of chlorite formation and the high values of Mg-octahedron. According to this assumption, we can calculate the amounts of MgO which were increased by chlorites formation and that by the increasing of Mg-octahedron and, moreover, the values of C. E. C. reduction corresponding to each of them.

On a stand basis of these assumptions we calculated the assumed pure states of the clays (A) quartz free basis, (B) quartz-kaolinite free state, and (C) quartz-kaolinite-brucite free state are shown in Table 1, respectively.

Although the last column (B) of non-treated clays and (C) of Mg-treated clays are assumed to be pure states, the figures of them may probably be considered as the idealized constituents of principal clays having dioctahedral character nearly in a pure state. If such a base for discussion can be accepted, several noticeable points may be interpreted as to be explained later. According to a comparison of the constituents of two calculated (B) in the cases of non-treated clays with two of (C) in the cases of Mg-treated clays, as a whole, all four clays are quite alike. The contents of Fe_2O_3 and K_2O are just the same before and after Mg-treatment, especially Fe_2O_3 are nearly equal in all of four clays. Variations appearing by Mg-treatment can be observed in that the contents of SiO_2 decreased about 3 per cent and MgO and H_2O^+ increased about 30 per cent and 20 per cent, respectively. Differences between the fine clays and the coarse clays are noticeable only in that the content of K_2O is larger and C. E. C. is smaller, accordingly, Na_2O is also smaller in the clays of the coarser clays than in that of the fine clays. Such figures probably show that two clays differing in their grain size are the same clay minerals and that alterations brought about by Mg-treatment would be merely a change in the octahedral layer where Mg-octahedrons were added, and the dropping of C. E. C. should be a natural result except for the new formation of small amounts of chlorites. Increases of H_2O^+ are considered to be due to increases of interlayer water as will be explained in the discussion.

Differential Thermal Analysis

For D. T. A. the samples were heated at the rate of 10°C per min. The results are shown in Fig. 1. As can be seen from the figures, no remarkable alterations can be detected on the curves of the clays treated with MgCl_2 . This may be an indication that Mg-treatment brought about no marked alteration on the principal clay portions. However, we can recognize several more or less indistinct variations such that the peak temperature of the second endothermic-peak migrated slightly toward a high temperature side by about 5°C and that the exothermic elevation of the curves from 230° to 360°C became less pronouncedly and the top at 325° or 330°C disappeared, consequently, it seems as if the top at 330° moved to 350° or 360°C . The former will be an indication that the crystal structure of these clays was altered to a somewhat highly stable condition by Mg-treatment, and from the latter we can consider that there would be some water loss in the range of temperature from 230° to 330°C and this may be an indication of the loss of increased interlayer water molecules. Furthermore, we recognize faint disturbances on the curves of Mg-treated samples in the range from 700° to 900°C . This may show the formation of a small amount of chloritic minerals by Mg-treatment.

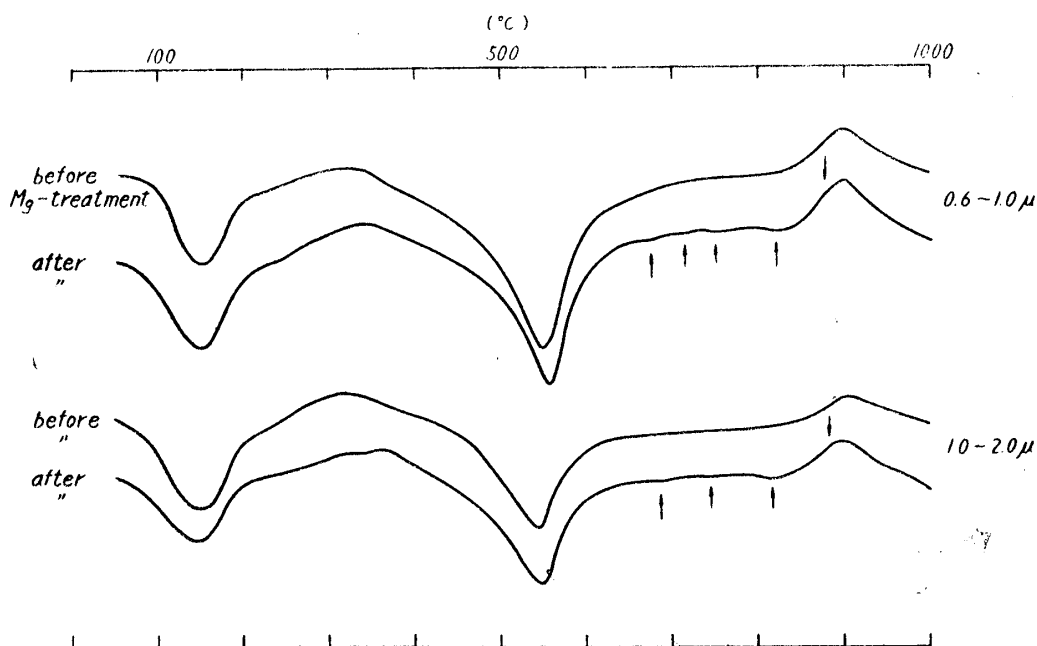


Fig. 1. D.T.A. curves of two clay fractions before and after treated with $MgCl_2$ -solution. \uparrow is showing the points of disturbance.

X-ray Diffraction Analysis

Two clay portions having different grain size were investigated before and after treatment with $MgCl_2$ solution using an automatic Geiger counting micrometer on exposure to a radiation of $Cu-K_{\alpha_1}$ rays. The results are shown in Fig. 2 and Fig. 3.

In Fig 2, we can observe high intensive diffractions which correspond to quartz and cristobalite such as 4.21, 4.05, 3.35 and 3.15 Å. Also, there are other diffractions of quartz and cristobalite smaller than 3 Å. From the intensity of the peaks at 4.21, 3.35 Å and 4.05, 3.15 Å we can determined the quantities of quartz and cristobalite as 12 per cent (0.6~1.0 μ) and 26 per cent (1.0~2.0 μ). The diffractions at 7.14, 3.57 and 1.483 Å are considered to be resulted from kaolinite of which amounts were determined as 32 per cent in both non-treated clays on the basis of quartz free state, it will correspond to 28.16 per cent (0.6~1.0 μ) and 23.68 per cent (1.0~2.0 μ) in the clays on a basis of the original samples.

We have reported on the principal portions of these clays in an other article (3) that they are swelling double-layer mica minerals similar to alleverdite. The variations of X-ray diffractions appearing by Mg-treatment can be observed in several points. Diffractions corresponding to 14.7 or 14.8 Å became more or less intense and the reflections at 7.35~7.45 Å, 4.74~4.80 Å, 4.30~4.31 Å and 3.59~3.60 Å appeared though they are not so intense. In addition, we can observe distinct reflections at 1.568 or 1.570 Å (in Fig 3) when treated with

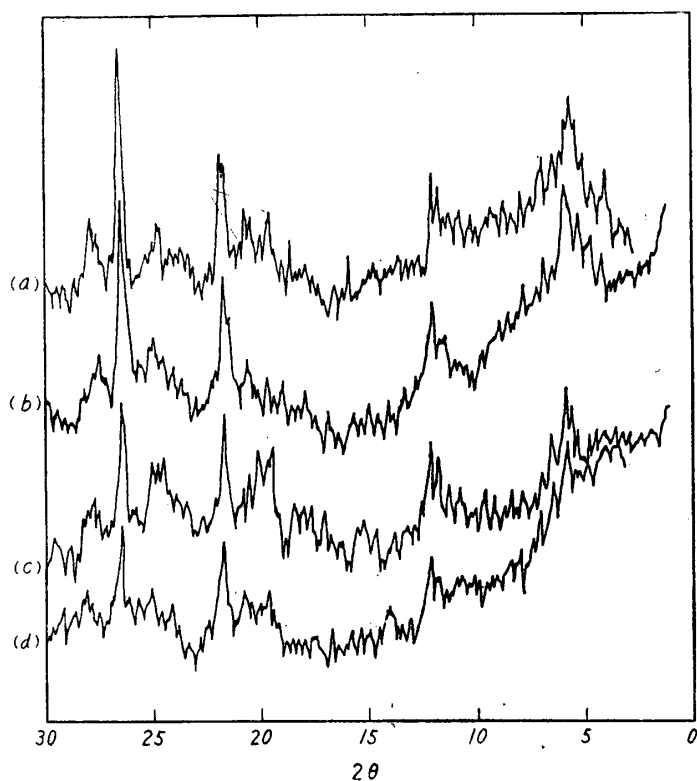


Fig. 2. X-ray diffraction micrograms of Na-clays in the angle region smaller than $2\theta = 30^\circ$

- (a) 1.0~2.0 μ fraction treated with $MgCl_2$ solution
- (b) 1.0~2.0 μ fraction non-treated with $MgCl_2$ solution
- (c) 0.6~1.0 μ fraction treated with $MgCl_2$ solution
- (d) 0.6~1.0 μ fraction non-treated with $MgCl_2$ solution.

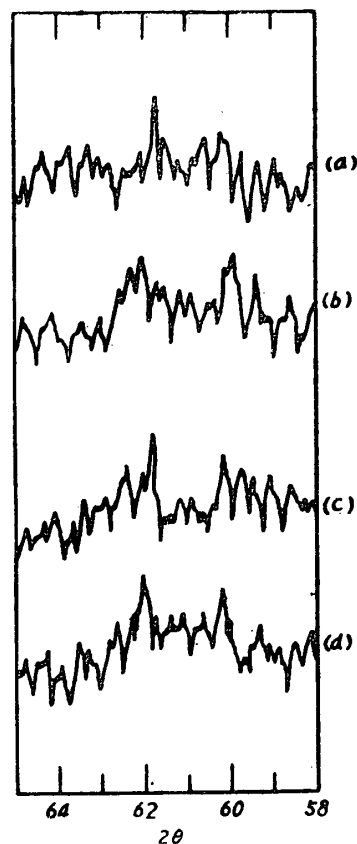


Fig. 3. X-ray diffraction micrograms of Na-clays in the angle region $2\theta = 58^\circ \sim 65^\circ$.

$MgCl_2$ but there is no such reflection peak in the cases of non-treated clays. These newly appeared reflections are considered to be a result of a new formation of chlorites or chloritic minerals, probably by adding of brucite layer. The reflection at 14.30 Å remained almost unaltered. We consider that this may be due to the double-layer mica minerals. This is slightly larger than $28.36 \pm 0.05/2$ of allevardite reported by Brindley (2), however, the difference may be due to the fact that the clays here studied contain far larger amounts of Fe_2O_3 and MgO than allevardite. In addition, we can detect a variation that the reflection at 4.50 Å or 4.51 Å migrated toward a slightly low angle side at nearly 4.505 Å and 4.515 Å, moreover, their intensities became stronger. When we examine reflections corresponding to the position of (060) in Fig. 3, it is clearly observed that the reflections at 1.499 and 1.502 Å in the case of non-treated clays moved to the positions of 1.518 Å and 1.505 Å. Such migration of reflection peaks by Mg-treatment would probably be induced by elongation of the length of unit cell structure in a direction of b-axis.

An elongation of b_0 -parameter can be brought about by an elongation of

either of tetra-layer or of octa-layer but it may also be possible by extending of both tetra- and octa-layers in the same time. Calculations on b_0 -parameters will be discussed later, but such variations of X-ray diffractions may be reasonable to be considered as a result of reaction between clays and Mg-ions.

The reflections at 14.30 Å and those of less intensity at 12.32 Å and 11.04 Å are considered to be (002) of 28.6, 24.6 and 22.1 Å which would be the basal reflections of double-layer micas having three, two, and one water layers per unit cell. If this is the case, in the clays here studied there may be three types of clays which differ in their activity to adsorb water on their clay surfaces such as mono-, di-, or tri-layers of water molecules against the same 50 per cent R. H. of atmosphere.

As a whole, we can say that there may occur no marked variation in the principal clay portions except for indications of newly formed chloritic minerals and those of faint alterations of reflections corresponding to (020) and (060) of dioctahedral 2:1 lattice minerals toward the lower angle side.

Discussion

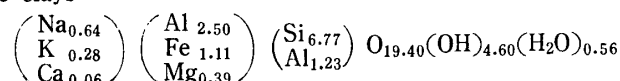
As we have already mentioned above, we proposed some assumptions for convenience to obtain an assumed pure state of clays and to consider alterations of clays after treatment with $MgCl_2$ solution. These assumptions may not necessarily be valid, however, it will make possible to construct structural formulas of clays before and after treatment with Mg-ions.

On the basis of chemical constituents ((B) and (C) in Table 1) of these clays calculated on assumed pure states such as quartz-kaolinite free non-treated clays and quartz-kaolinite-brucite free basis for Mg-treated clays we can construct the structural formulas of clays. The structural formulas of these four clays thus obtained are shown in Table 2. It can be seen from the figures in Table 2 that all four clays are quite similar and nearly alike that of alleverdite. They varied from alleverdite in that less Al-substitution in a tetra-layer, far larger amounts of Fe- and Mg-atoms in an octalayer, and that the amount of interlayer water molecules is slightly less in the clays of 1.0~2.0 μ though that of the finer clays is quite the same. The variations appeared by Mg-treatment are observed in the slightly increase of Al-substitution in a tetra-layer, an increase of Mg-atoms in an octa-layer, a marked increase in the amount of interlayer water, and an increase of Ca-atoms and a decrease of Na-atoms in forms of cations exchangeable or non-exchangeable. It must be noticed that the numbers of Mg-atoms in an octalayer increased but the total positive charges of cations in an octalayer did not increase materially. If it is valid that negative charges of the whole cell are not altered and its amount is 43.4 per unit cell such as $O_{18.40}(OH)_{4.60}$, increased Mg-atoms through entering into an octalayer did not increase the total numbers of cations in an octalayer but

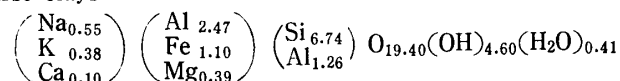
Table 2. Structural Formula of the Clays before and after treated with $MgCl_2$ and that of Allevardite.

(I) Before Mg-treatment

Fine clays

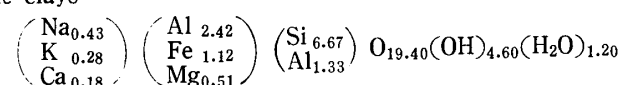


Coarse clays

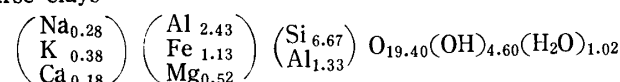


(II) After Mg-treatment

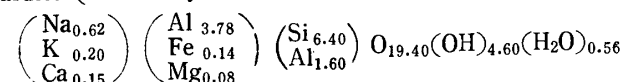
Fine clays



Coarse clays



(III) Allevardite (Double-layer mica mineral)



they would at least introduced an elongation of b_0 -parameter of an octalyer.

Here, when we calculate the magnitudes of elongations of b_0 -parameters after Mg-treatment using the data of the structural formulas thus obtained they will become 0.0229\AA ($0.6\sim 1.0\mu$) and 0.0171\AA ($1.0\sim 2.0\mu$) provided elongations of b_0 by one atom of Al-substitution for Si is 0.123\AA and that of one Mg-atom octahedron is 0.066\AA . The migrations of X-ray diffraction at (060) measured by the experimental results are 0.0038\AA ($0.6\sim 1.0\mu$) and 0.0028\AA ($1.0\sim 2.0\mu$), thus these values correspond to 0.0228\AA and 0.0168\AA of (010), respectively. The values calculated from the structural formulas and those obtained by measurements of X-ray diffraction data nearly coincide. When a migration of X-ray diffraction at (060) is 0.001\AA toward a lower angle side and this is brought about by only an increase of Mg-octahedron the content of MgO should have increased 0.48 per cent and a reduction of C. E. C. must be 23.9 me. per 100 g clays. Thus it follows that the reductions of C. E. C. corresponding to the amounts of migrations of X-ray diffractions such as 0.023\AA and 0.017\AA are 90.8 and 66.9 me. when calculated as 100 per cent pure clays and they are far larger than the actual reductions of C. E. C. 17.7 me. and 14.4 me. in the cases of original clays. Consequently, elongations of b_0 -parameter must contain those by some other origins and we will consider it as due to the influence of extending of tetralayer in them. If this is the case, an increase of Al-tetrahedrons would be induced by an expelling action of increased Mg-octahedrons. This will lead to a consideration that highly active Mg-ions in a outer medium solution possess a tendency to expel some of Al-octahedron

into a Si-tetralayer but not affect Fe-octahedrons. It may be reasonably understood because Fe-atom can not enter into Si-tetralayer owing to their radius being too large to fit in a position of Si-tetrahedron.

A question may arise why Al-substitutions can not proceed farther than the actual degree of the experimented result such as 1.33 even when an action of very high activity of Mg-ions had operated. We can explain it through the fact that there are several limiting points to inhibit a progress of Al-substitution where clay structure become more stable. These points of Al-substitution should be that where a Al-substitution reaches to the numbers of $n \times 0.334$ when $n =$ an integral. On the problem and about its reason the senior author has already given explanations and discussions in an other article (1). The reason that Al-substitution in the case of our experiments had stopped at the point of 1.33 can be explained as the original Al-substitution of 1.23 or 1.26 had started to increase but was stopped at $0.334 \times 4 = 1.332$ or 1.33. The points of 1.23 or 1.26 are larger than the stable point of $0.334 \times 3 = 1.002$, then the crystal of the original clays would possess some irregularity or weakness in their structures and accordingly would be affected by Mg-ions toward a direction of progress of Al-substitution. However, it must be considered that Al-substitution in a Si-tetralayer can be influenced by environmental actions towards either an increasing or a decreasing direction. Thus the clays having Al-substitution number of $n = 0.334$ where n is a decimal number will alter their structures to high or low substitution-types according to the acting forces. Furthermore, there is one point of balancicity between length of tetra- and octa-layers altered through actions of the environmental forces. When there exist more space in an octalayer to receive more octahedrons for the balance between two of tetra- and octa-layers these unbalance would favor to introduce an increase of Mg-octahedrons but when there is no such space these alterations can not occur. Consequently, we can conclude that when there are some irregularity or unbalance or space room in a lattice structure active Mg-ions can enter into the octalayer and expel some Al-octahedrons into a Si-tetralayer until a certain point of stable structure is obtained.

The other point to be noticed is a marked increase of water contents induced by Mg-treatment. The large content of water in the crystal structure of double-layer mica minerals is explained by Brindley as an interlayer water, and its amount is 0.56 mols in alleverdite, however, in the present clays, an increase of these water are as high as about twice the original clays. Are there any space room for receiving those water between two mica units? If we assume that the area of clay surface of the basal plane occupied by fixed non-exchangeable cations is proportional to the ratio of their valences divided by negative charges produced by numbers of Al-substitutions in a tetralayer, then, in the case of alleverdite, the ratio of the area of the basal

plane occupied by fixed cations to the total basal plane per unit cell will be obtained when the equivalents of cations fixed is divided by the equivalents of negative charges by Al-substitution, $0.50/1.60 = 31.2$ per cent of the whole surface area of the basal plane per unit cell. Accordingly, the area not occupied by cations, that is, a vacant place area possible to receive water molecules is 68.8 per cent. When the surface area of alleverdite per unit cell is assumed to be about 47 \AA^2 the vacant area would be $47 \times 0.668 = 32.34 \text{ \AA}^2$. Molecules of interlayer water are 0.56 per unit cell, but the interlayer vacant place is only one per two mica units, thus the area occupied by interlayer water molecules should be twice much, or $10.5 \times (0.56 \times 2) = 11.76 \text{ \AA}^2$ provided the area of one water molecule is 10.5 \AA^2 . Consequently, the ratio of the area occupied by interlayer water against the area not occupied by cations, to say, vacant for receiving of water may be as follows:

$$\frac{0.56 \times 2 \times 10.5}{47 \times 0.688} = 36.0 \text{ per cent}$$

In the case of non-treated clays here studied, on the basis of calculated pure state in Table 2, the interlayer water are 0.56 mol ($0.6 \sim 1.0 \mu$) and 0.41 mol ($1.0 \sim 2.0 \mu$). The ratio of the area occupied by water against the area of the vacant space not occupied by cations calculated by the same way as above mentioned will be as follows:

$$\text{fine clays } (0.6 \sim 1.0 \mu) \quad \frac{10.5 \times 0.56 \times 2}{48 \times 0.675} = 36.5 \text{ per cent}$$

$$\text{coarse clays } (1.0 \sim 2.0 \mu) \quad \frac{10.5 \times 0.41 \times 2}{48 \times 0.54} = 33.2 \text{ per cent}$$

Here, we assumed an area of our clays to be 48 \AA^2 because they contain more Fe- and Mg-atoms, accordingly, a_0 and b_0 of the clays would be larger than alleverdite. The obtained figures are both nearly equal to that of alleverdite and all of these three clays show that about one-third portions of the vacant spaces are occupied by interlayer water.

On the contrary, in the cases of clays treated with MgCl_2 , the surface area not occupied by fixed cations are 52.0 per cent ($0.6 \sim 1.0 \mu$) and 44.5 per cent ($1.0 \sim 2.0 \mu$) of the whole surface area. The ratio of the area occupied by water against the vacant area will become just 100 per cent as;

$$\text{fine clays } (0.6 \sim 1.0 \mu) \quad \frac{10.5 \times 1.20 \times 2}{48 \times 0.519} = 100.8 \text{ per cent}$$

$$\text{coarse clays } (1.0 \sim 2.0 \mu) \quad \frac{10.5 \times 1.02 \times 2}{48 \times 0.445} = 100.3 \text{ per cent}$$

Then, we consider that an increase of interlayer water would be proceeded by boiling with MgCl_2 solution just to reach the point where the whole interlayer

surface areas not occupied by fixed cations are fulfilled with water.

As whether such an increase of interlayer water was influenced by the presence of Mg-ions or not, we consider it may be done quite independently. However, it is interesting that these interlayer water molecules between two mica units are held very tightly as high as 100 per cent and could not be expelled even when heated at 240°C for eight hours. This will suggest the presence of certain forces attracting water molecules between two units which are stronger than the usual forces adsorbing water molecules onto a surface of clay minerals. With regard to this point we can consider the presence of hydrogen-bond linkages between an interlayer water molecule and two surface oxygen planes of tetralayer of clay units when new Al-tetrahedron was increased from a octalayer because the distance between two mica units may be too narrow to permit the entrance of both cations such as Mg-ions and their hydration water but hardly enough in width to permit the entrance of water molecules in thickness of only one layer. This may be not so illogical because there exist already some water about one-third of the whole area.

A reaction to form chloritic triocta-minerals through contraction of brucite layer proceeded only to a small extent. Considering from this it is clear that a reaction to form chlorites is limited to the extent which corresponds to the amount of triocta-layer 2:1 lattice minerals such as hydrobiotite or vermiculitic clays present and do not proceed further. Dioctahedral 2:1 lattice type mica is considered to be unable to react with a brucite layer.

The marked dropping of C. E. C. which occurred after treating with Mg-ions can not be interpreted exactly because the assumed calculations used here are not satisfactorily correct. Furthermore, the presence of a few per cent of trioctahedral clays is neglected in calculations, thus, some errors may be introduced in the values of the structural formulas. In spite of these incorrectness, we are able to detect an increase of the total numbers of cations in an octalayer though it is very small, and they become slightly over than 4.0, on the other hand, Al-substitution numbers in a tetralayer also increased, accordingly, the total negative charges did not decreased to a marked degree but remained practically unaltered as before. However, in this case, the negative charges produced by increased Al-substitution were unable to act as actual attracting forces against cations in a solution owing to narrowness of width of an interlayer opening. This may plays a role of an important part in the reduction of C. E. C. There is another unexplainable fact for C. E. C. dropping that the amount of Ca-atoms in a unit cell increased after Mg-treatment inspite of no supplying of Ca-ions during the reaction with Mg-ions and in the course of procedures of preparation of samples. The amounts of increased Ca-atoms are so large as impossible to neglect and these amounts correspond to a considerable portion of the reduced C. E. C. In the values of structural formulas indicated

in Table 2 this plays an important role in the counteraction of negative charges. However, at the present stage of our knowledges we can not interpret the reason for the real origin of CaO increased and how they effectively influence the clay structure. The problem must be reserved for future studies.

Summary

We have already studied on the clay minerals separated from a paddy soil. The clays, especially those having more or less large grain sizes such as $0.6 \sim 2.0\mu$, contain relatively low contents of MgO and K_2O but large amounts of loss on ignition over $240^\circ C$. On account of showing long series of X-ray diffractions as 28.6, 24.6, 14.3, 12.3 \AA we defined them as double-layer mica minerals which resemble allevardite.

We have examined the influences of Mg-ions upon these clays through alterations appeared after treatment with N-MgCl₂ solution chemically, D.T.A. and by X-ray diffraction analysis.

Distinct variations are a decrease of SiO₂, but relatively small, a marked reduction of C. E. C. and increases of MgO, CaO and H₂O⁺. An increase of MgO is attributed to the formation of small amounts of chloritic triocta-minerals, and an extending of b_0 -parameter is attributed to a result of increasing of Mg-octahedrons. Dropping of C. E. C. is considered to be due to an increase of Mg-octahedron, at least, its larger part would be so and a small part would be introduced by chloritic brucite-layer. Decrease of SiO₂ can be brought about by an increase of Al-tetrahedrons which are inevitably transported from octahedral Al-atoms by the expelling action of Mg-octahedron increased. Marked increases of H₂O⁺ is interpreted as an increase of interlayer water molecules and is explained through calculations of areas that the interlayer vacant surface area not occupied by fixed cations, K + Ca, is fulfilled by water as high as 100 per cent. However, the question remains on an increase of CaO in spite of no supplying and on the role of Ca-ions influencing upon reduction of C. E. C.

References

- 1) Uchiyama, N. (1956). Tohoku J. Agr. Res., **7**, 1.
- 2) Brindley, G. W. (1956). Amer. Min., **41**, 91.
- 3) Uchiyama, N. and Onikura, Y. (1956). Tohoku J. Agr. Res., **7**, 8.