Flash Dehydroxylation of Montmorillonite

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Abstract

The effect of flash decrease of pressure on the dehydroxylation process of montmorillonite (Yamagata Prefecture, Japan) was studied. The experimental technique based on flash dehydroxylation means that the sample under atmospheric pressure was transferred to vacuum in a moment. The properties of flash dehydroxylation sample and the heating samples under constant pressure were investigated by means of X-ray, DTA, TG, and IR, etc. .

The dehydroxylation temperature of lattice water was shifted to lower temperature with the decreasing pressure. The time for diffusion process of water molecules accompanied with dehydroxylation was rapidly redued below 100 mmHg. The basal spacing of two heating samples under constant pressure gave 9.73 Å and that of flash dehydroxylation sample gave 9.60Å. The gap of 0.13Å might depend on the different shift of potassium ion situated between the crystal layer. Namely, the exchangeable cation which occupied the space between the crystal sheets just before dehydroxylation shifted into vacant space in silicon-oxygen sheet which had come from dehydroxylation by means of flash pressure change. New pattern of 20—26 Å were appeared in X-ray diffraction of flash dehydroxylation samples prepared by alkali-treatment. The influence of the water molecules diffusion on crystal structure of montmorillonite might be minimized by flash change of pressure.

1. Introduction

There have been many investigations on the dehydration phenomena of clay minerals under constant pressure. Murray and White[1], Allison[2], Vaughan[3], and Tuzuki and Nagasawa[4] studied the kinetics of decomposition of clay minerals. Murray and White measured the rates of isothermal dehydration of clay and calculated the kinetic constants of the materials. They found that the first order reaction law was obeyed over $80-90\%$ of the decomposition range. Evan and White[5], Brindley and Nakahira[6], and Murray etc., also studied the dehydration process. According to Evan and White, in the montmorillonite lattice the OH ions occured in the two oxygen sheets of the octahedral layer and the reaction could be written as

$$(OH^-)_2 = H_2O + O^{2-}$$
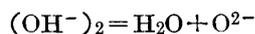
Brindley and Nakahira regarded the reaction as

$$OH + OH = (OH)^* + (OH)^* \rightarrow H_2O\uparrow + O$$

$$(OH)^* : \text{activated state.}$$
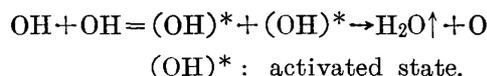
They also pointed out the importance of vapour pressure on dehydration mechanism. Avrami[7] studied the rate of nucleation during decomposition and Kopsted[8], Giess[9], Sharp[10] derivated

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the equation of solid state reaction on assumption of some process. Holt, Cutler and Wadsworth[11] studied the kinetics of decomposition of kaolinite under 1-10 μHg.

Above work have been investigated under constant pressure, but there was no work for the dehydration of montmorillonite by means of flash pressure change near dehydration temperature.

The dehydroxylation process of clay minerals involve the following steps.
1. formation of nucleation and growth.
2. diffusion of water molecules through the channel of crystal structure.
3. dispersion of water molecules from crystal edge.
4. diffusion of water molecules through the opening between grains.
5. rearrangement of crystal lattice (exothermic reaction).

Among above steps, the steps of 2—4 are related to the method of flash pressure change. This report have been undertaken to study the effect of flash pressure change on dehydroxylation process of montmorillonite.

2. Specimen and Method

Specimen : The purified montmorillonite from Geppu, Yamagata Prefecture, Japan, was ground to the grain size of 100—200 mesh and dried at 200°C to dehydrate the adsorbed and interlayer water. The samples treated for 1—6 hours by 5N NaOH at 80°C, neutralized by 10 % H_2SO_4 and washed by distilled water were also used for dehydration study. The alkali-treatment was carried out for the removal of silica which was naturally involved in montmorillonite as impurities or was independent of montmorillonite crystal structure.

Apparatus : Flash dehydroxylation study was carried out using the apparatus illustrated in Fig. 1. The apparatus consists of vessel in which the samples are set, a reducing pressure
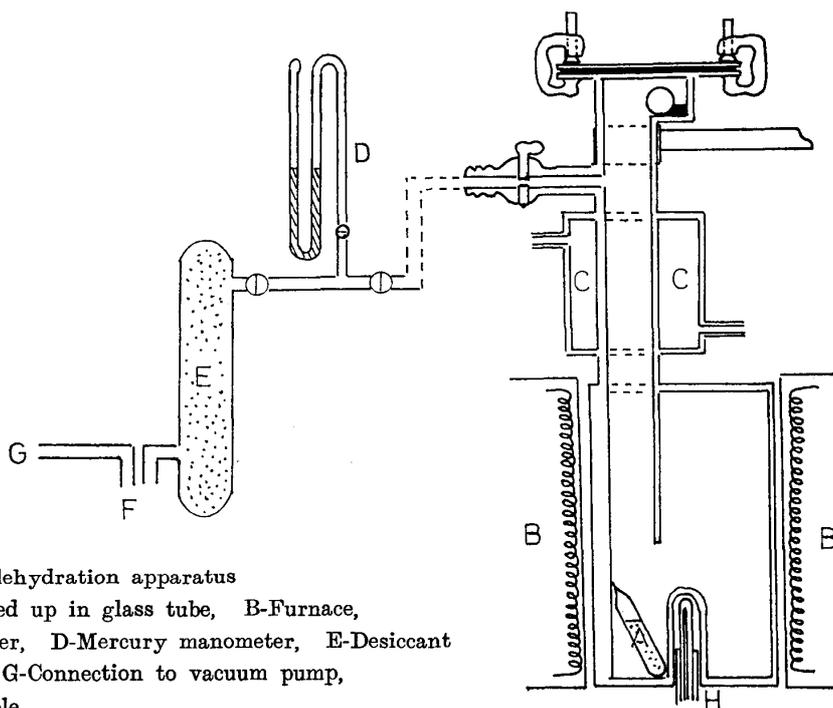

Fig. 1 Flash dehydration apparatus
A-Sample sealed up in glass tube, B-Furnace,
C-Cooling water, D-Mercury manometer, E-Desiccant
F-Gas tank, G-Connection to vacuum pump,
H-Thermocouple

equipment and a vertical nicrome-wound furnace. The sample vessel had the volume of $800 \, cm^3$ and the sample sealed in glass tube was set on the bottom of the vessel. The inner pressure of the vessel could be reduced to $1 \, mmHg$. The sample vessel was set into furnace and heated by heating rate of $10°C$ per minute.

Method of flash pressure change : The dehydration samples of three categories were prepared by following technique.

"Flash dehydroxylation sample"

The glass tube in which the sample was sealed up was set on the bottom of the sample vessel (reference Fig. 1) and the inner pressure of the vessel was reduced to $2 \, mmHg$. Then the sample in glass tube was heated to dehydroxylation temperature $670°C$. At this temperature a steel ball set on the upper part of the sample vessel was dropped, so that the glass tube cracked and the sample under atomospheric pressure scatterred into vacuum in a moment. Authors named the material maked by this method as the flash dehydroxylation sample.

"Heating sample under reduced pressure"

The sample was scattered into vacuum at room temperature and then heated to $670°C$ in apparatus.

"Heating sample"

The sample was set in sample vessel at room temperature and heated to $670°C$ under atomospheric pressure.

The physico-chemical properties of these dehydoxylation samples were investigated by means of X-ray, DTA, TG, and IR, etc..

3. Results and Discussion

3·1 The relation between condition of pressure and dehydration temperature.

The relation between condition of pressure and dehydration temperature of montmorillonite was indicated in Fig. 2. The temperature of maximum deflection in differential thermal analysis at which the reaction rate is maximum was shifted to lower temperature with decreasing pressure. The peak temperature of DTG curve ran parallel to the peak temperature of DTA curve with decreasing pressure and below $100 \, mmHg$ it became rapidly low approaching to peak temperature of DTA curve. From the results it is assumed that the diffusion time of water molecules through channel of crystal structure was shortened with further decreasing pressure, as the pressure was reduced below $100 \, mmHg$, namely the water molecules radiated out of crystal more speedily. It seems that the forming rate of nucleus in crystal was also more increased, since vapour pressure in crystal was more decreased. At the point A of intersection, there might be no diffusion process. It is assumed that the pressure at this point was at least below $1 \, \mu Hg$, for Holt etc. reported that the rate of reation increased with decreasing pressure under $1—10 \, \mu Hg$.

The heat of dehydration was calculated $455 \, cal/g$ using Claperon-Clausius equation. Basing on the equation derivated by Freeman and Carroll[12], $\triangle \log. \, dw/dt / \triangle \log. \, Wr$ vs $\triangle(T^{-1}) / \triangle \log. \, Wr$ was plotted and from a slope the activation energy was calculated $53 \, Kcal/mole$ and from intercept the reaction was first order.
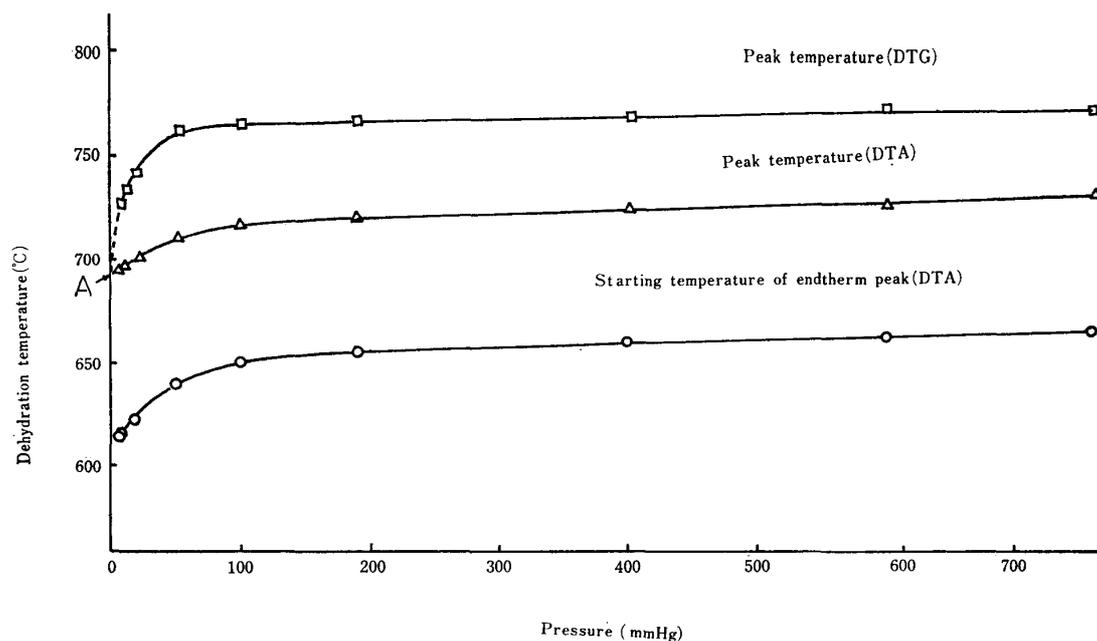
Fig. 2 Relation between pressure and dehydroxylation temperature of montmorillonite

3·2 The change of (00ℓ) reflection in X-ray diffraction.

There was no change in X-ray powder diffraction except that the c dimension was shifted from 14.9 Å to 12.3 Å and the pattern was slightly reduced in intensity due to dehydration of adsorbed and interlayer water. Some structural change took place with the lose of the hydroxyl group, as would be expected, such that the pattern intensity at 12 Å of (001) reflection was reduced gradually and one at 9.8 Å was increased in oppsition. The (00ℓ) reflection of dehydroxylation sample was considerably reduced in intensity comparing with that of original sample. Since the sample just before dehydration gave the basal spacing of 12.3 Å, it was expected that there were the adsorbed ions between the crystal sheets. The cations would be shifted into vacant spaces in tetrahedral layer or on the basin of the hexagonal network with advance of dehydroxylation reaction, so that montmorillonite would turn to the structure which had been referred to by Bradley and Grim[13] as the anhydrous phase of montmorillonite.

3·3 The effect of flash pressure change.

The X-ray diffraction pattern of dehydration samples of three categories gave no difference except the intensity and values of (00ℓ) reflection. The (001) reflection of each dehydration sample was shown in Fig. 3. Though (001) reflection of the flash dehydroxylation sample gave 9.6 Å. The pattern of the flash dehydroxylation sample showed the very sharp and symmetrical peak comparing with that of the two heating sample. The pattern of the flash dehydroxylation sample was reduced only in intensity slightly comparing with that of the sample just before dehxdroxylation. Namely it is assumed that the diffusion of water molecules through opening of crystal structure were minimized by mean of flash change of pressure. So the layer structure of flash dehydroxylation sample was piled up more regularly than that of heating samples.

The average basal spacings of two heating samples under constant pressure were calculated 9.73 Å. On the other hand, that of flash dehydroxylation sample gave 9.60 Å. Since there
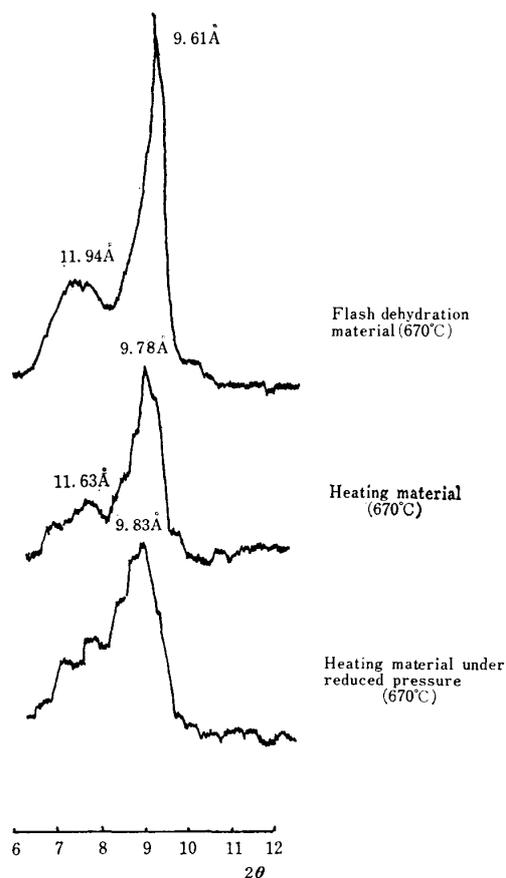
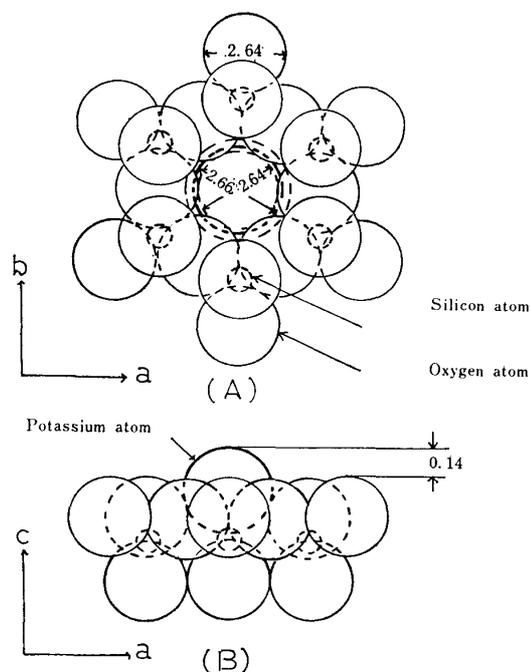Fig. 3 X-ray diffraction pattern of various
dehydration samples

Fig. 4 Hexagonal arrangement of silicon-oxygen
tetrahedra in a silica sheet

Table 1 Chemical composition of montmorillonite from Geppu, Yamagata Prefecture, Japan. [14]

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Ig. loss	Total
75.01	0.10	12.75	1.41	1.00	1.04	2.63	1.04	4.72	99.70

were no difference between two heating samples and the flash dehydroxylation sample about infrared spectra or intensity and disorder at larger angle side of (02, 11) reflection, the difference of 0.13Å (9.73—9.60 Å) might be due to interlayer distance. Basing on the result of chemical analysis illustrated in Table 1, Na^+ (ionic diameter 1.94 Å), K^+ (2.66 Å), Ca^{2+} (1.98 Å), Mg^{2+} (1.32 Å) could be regarded as the exchangeable cations. The relation between exchangeable cation and silicon-oxygen tetrahedral sheet was shown in Fig. 4. The reserve side of paper was the surface of crystal layer in Fig. 4 A. After dehydroxylation there would leave the vacant space of diameter 3.48 Å which was shown by adotted larger circle. The exchangeable cation would pass through a hollow which was shown by the dotted smaller circle to drop into above vacant space. The cation such as Na^+, Ca^{+2}, Mg^{2+} would be able to pass through this hollow, but K ion would be unable to pass and be fixed on the basin of hexagonal network, for potassium diameter is larger than the diameter of the hollow by 0.02Å. On this occation, potassium ion would have the 0.14Å projection from the layer surface (reference Fig. 4 B).

So the basal spacing (L) of two ordinary heating samples were given by

$$L = 9.57\,\text{Å} + 0.14\,\text{Å} = 9.71\,\text{Å}$$

$9.57\,\text{Å}$ in above equation was the theoretical value of basal spacing. As the observed basal spacing of the heating samples were $9.73\,\text{Å}$, there left $0.02\,\text{Å}$. $9.57\,\text{Å}$ was the value in case that lattice layer was ideally piled up, and actually the pile of layer had the irregular displacement of $\pm nb/3$ in direction of **b** axis. The gap of $0.02\,\text{Å}$ might depend on these irregular displacement. The basal spacing of the flash dehydroxylation sample similarly involved the gap of $0.02\,\text{Å}$. The value of $9.73\,\text{Å}$, however, was the averrage of various basal spacing, for the (00ℓ) reflection was broad. In the case of flash change of pressure, it is assumed that potassium ion occupied the basin would be shifted into vacant spaces in silicon-oxygen sheet which came from dehydroxylation, because a large number of water molecules rapidly passed through interlayer between the crystal sheets in a moment. These phenomena were also expected by the fact that cation exchange capacity of the flash dehydroxylation sample was extremely smaller than that of two ordinary heating samples (reference Table 2). Since the flash dehydroxylation sample had not the projection from layer surface, the basal spacing was narrower than that of two heating samples by $0.13\,\text{Å}$. Depending on TG, the flash dehydroxylation sample had yet 41 per cent of lattice water. The water molecules dehydrated with flash change of pressure needed to have already formated in crystal directly before the flash change of pressure was done. So the rate of for-

Table 2 The cation exchange capacity of two dehydroxylated materials

Sample	C.E.C(meq/100g)
flash dehydration material	18
heating material	80

mation of nucleus which might be involve (OH)* according to Brindley and Nakahira or (OH)⁻ ion according to Evan and White was 59 % in all. These statement was supported by a fact that the amount of water loss of the flash dehydroxylation sample almost corresponded with that of heating sample.

It seems that the dehydration reaction was taken place more easily with the removal of silica in tetrahedral layer by alkali-treatment. So the sample treated by alkali was used for the flash dehydroxylation. The X-ray powder data of flash dehydroxylation sample were illustrated in Table 3. The (02, 11) reflection's intensity of each sample were regarded as Io. The (00ℓ) reflection of alkali sample by flash pressure change was reduced in intensity with increase of treated time. This phenomenon was also observed on the samples before dehydration. It is worthy of notice that there appeared new pattern of 20—$26\,\text{Å}$ in X-ray diffraction of flash dehydroxylation samples prepared by alkali-treatment. The heating samples under constant pressure did not give the new pattern. The intensity of new pattern of 1—3 hours alkali-treatment samples was reduced reversely. The sample, of which layer structure was completely broken down by further alkali-treatment, did not give this pattern. Since new pattern was influenced with heating and ethylene glycol treatment, it was probably the reflection caused by the sheet parallel to the direction of **a** and **b** axises. The flash dehydroxylation treated for 1 hour by 7N and 10N NaOH at 80°C gave also the new pattern of $22\,\text{Å}$. Infrared absorption spectra in the region 1600—600 cm⁻¹ were shown in Fig. 5. In the case of the sample b treated by alkali for 3 hours comparing with original sample c, the band due to Si-O at 790 cm⁻¹, the

Table 3 X-ray powder date of flash dehydroxylation samples treated for various **times** by 5N NaOH.

(hkl)	1 hour d Å	I/I_0	2 hours d Å	I/I_0	3 hours d Å	I/I_0	4 hours d Å	I/I_0	5 hours d/Å	I/I_0	6 hours d Å	I/I_0
	21.0	3	23.9	2	26.0	3	26.0	6	23.9	3	19.2	3
(001)	9.60	15	9.60	6	9.60	6	9.60	6	9.60	3	9.60	3
(002)	4.77	6	4.77	3	4.77	4	4.77	3	4.77	3	4.77	3
(02 11)	4.46	10	4.46	10	4.46	10	4.46	10	4.46	10	4.46	10
(003)	3.16	17	3.16	6	3.20	6	3.18	5	3.18	5	3.18	5
(-)	2.53	9	2.52	8	2.52	9	2.51	9	2.52	5	2.53	5
(005)	1.90	2										
(24 15)	1.68	2	1.68	2	1.68	2	1.68	2	1.68	1	1.68	1
(06 33)	1.50	2	1.50	2	1.50	1	1.50	1	1.50	1	1.50	1
(40 26)	1.29	1	1.29	1	1.29	1	1.29	1	1.29	1	1.29	1

shoulder at $1130 cm^{-1}$ and the band due to Si-O, Al-O at $1100—1000 cm^{-1}$ were reduced in intensity. Since the intensity of X-ray diffraction or infrared spectra of samples treated by alkali over three hours were suddenly reduced, it seems that free silica involved in montmorillonite were removed away with alkali-treatment till three hours and over three hours the removal of the silica in tetrahedral layer of montmorillonite began to take place by alkali-treatment. These phenomena would have relations with the maximum intensity of new pattern of the samples treated for 3 and 4 hours.

Fig. 5 Variation of infrared spectra $(1600\sim600 cm^{-1}rang)$ of flash dehydroxylation samples
a : sample treated by 5N NaOH for 6 hours
b : sample treated by 5N NaOH for 3 hours
c : original sample

The water molecules might pass through the hexagonal vacant space surrounded with oxygen atoms in silicon-oxygen sheet (reference Fig. 4) and break abruptly into interlayer between the crystal layer. Since there occured the high pressure gap between inside and surface of crystal in a moment of flash decrease of pressure, the water molecules passed through interlayer between crystal sheets with the flow (Q) indicated as Knudsen flow of following formula and scattered out of clay crystal.

$$Q = \frac{4}{3} \pi \frac{a}{1} \sqrt{\frac{2KT}{\pi m}} \ (P_1 - P_2)$$

a : radius of tube, 1 : length of tube, K : boltzman constant,
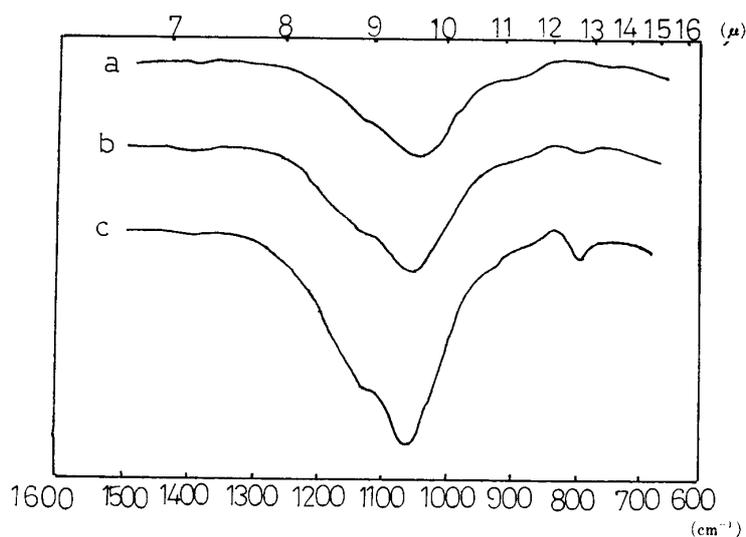T : absolute temperature, m : weight of molecule

Thus, the influence of the diffusion of water molecules were minimized by means of flash change of pressure. This, however, would be true in only case that the amount of water loss are small and the structure of crystal is porous to some extent, in other word, there are enough space in crystal for water molecules to pass through. In other case that crystal structure is close and the amount of water loss are much, the crystal will be completely broken down by the great flow of water molecules in a moment.

4. Summary

(1) The temperature at which the dehydration reaction rate is maximum was shifted to lower temperature correlating with decreasing pressure. The diffusion process of water molecules through channel of crystal structure rapidly began to shorten below 100 mmHg.

(2) The basal spacing of two heating samples under constant pressure gave 9.73 Å and that of flash dehydroxylation sample gave 9.60 Å. The gap of 0.13 Å might depend on the different shift of potassium ion situated between the crystal layers. Namely, the exchangeable cation which occupied the space between the crystal sheets just before dehydration shifted into vacant space in silicon-oxygen sheet which had come from dehydration by means of flash pressure change.

(3) The flash dehydroxylation samples prepared by alkali-treatment gave new pattern of 20—26 Å caused by the sheet parallel to the direction of **a** and **b** axises in X-ray diffraction.

(4) The pattern of (00ℓ) reflection of flash dehydroxylation sample showed the very sharp and symmetrical peak comparing with that of two heating samples. So in a case that the crystal structure is porous to some extent and the amount of water loss are small, the influence of the water molecules diffusion on crystal structure may be minimized by means of flash change of pressure.

Reference

1) Murray P. and White J., Tras. Brit. Ceram. Soc., 48, 187 (1949) ; ibid. 54, 151 (1955).

2) Allison F. B., Clay Minerals Bull., Mineralogical Soc., 2, 242 (1955).

3) Vaughan F: ibid., 2, 265 (1955).

4) Tuzuki Y. and Nagasawa T., "Progress of Clay Sci. Vol. 1" Gihodo Pub. (1959) p.144.

5) Evan J. L. and White J., Tras. Brit. Ceram. Soc., 57, 289 (1958).

6) Brindley G. W. and Nakahira M., "Clay and Clay Minerals Proc. 5th Natl. Conf." Acad. Sci. Pub. (1956) p.266.

7) Avrami M., J. Chem. Phys., 7, 1103 (1939) ; ibid. 8, 212 (1940) ; ibid. 9, 177 (1941).

8) Kopstad P., Nature, 179, 1362 (1963).

9) Giess E. A., J. Am. Ceram. Soc., 46, 374 (1963).

10) Sharp J. H., Brindley C. W. and Narahari Achar, B. N., J. Am. Ceram. Soc., 49, 379 (1966).

11) Holt J. B., Cutler I. B. and Wadsworth, M. E., J. Am. Ceram. Soc., 45, 133 (1962).

12) Freeman E. S. and Carroll B. J., Phys. Chem., 62, 394 (1956).

13) Grim R. E. and Bradley W. E., Am. Mineral., 33, 50 (1948) ; ibid 36, 182 (1951) ; J. Am. Ceram. Soc., 23, 242 (1940) ; Grim R. E., Am. Mineral., 46, 1329 (1961)., Clay Mineralogy. (Macmillan) (1953).

14) "Clay Handbook", Clay Sci. Japan Pub. (1967) p.233.