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THE STUDY OF CLAY MINERALS BY SMALL-ANGLE X-RAY SCATTERING

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ABSTRACT

Small-angle scattering of X rays by three kinds of clay minerals (allophane, hydrated halloysite and kaolinite) was observed over scattering angles from 8′ to 70′, in the range below 275 Å in radius of gyration, and was analyzed by Jellinek-Solomon-Fankuchen's method and Porod's theory. Jellinek-Solomon-Fankuchen's method for hydrated halloysite and kaolinite showed the largest value of the distribution function $M(\overline{Rg})$ occurring in the range more than 275 Å in radius of gyration. However, for allophane the largest value of $M(\overline{Rg})$ occurred at the smallest radius of gyration. Porod's theory was applicable to hydrated halloysite and kaolinite, but not to allophane. The average value of the radius of gyration $\langle\overline{Rg}\rangle$, or the "extent of coherence" lc, was in good agreement with particle size estimated from electron micrographs, only for allophane. For hydrated halloysite $\langle\overline{Rg}\rangle$ and lc were smaller than those of heated halloysite. After grinding, the values of $\langle\overline{Rg}\rangle$ and lc of allophane increased and the "structure index" f decreased.

INTRODUCTION

Clay minerals are one of the materials which give small-angle scattering of X rays. This phenomenon of scattering has been investigated by many authors to measure the size of particles in the region below 1,000 Å. West (1952) studied clay suspensions in water. Arnott (1965) determined the particle size of clay minerals by Shull-Roess' method (1947), revealing that the average diameter of clay mineral was in good agreement with the particle size observed by electron microscopy. However, interpretation of the small-angle scattering by clay minerals is still under discussion. In the present study, the measurement of particle size and its distribution were examined on the basis of the theories of Jellinek-Solomon-Fankuchen and Porod.

According to Jellinek-Solomon-Fankuchen (1946), if a discrete distribution is assumed, the scattering intensity will be expressed as

$$I(h) = K\sum_i M(\overline{Rg}\cdot i)(\overline{Rg}\cdot i)^3 \exp\left(-\frac{h^2(\overline{Rg}\cdot i)^2}{3}\right) \qquad (1)$$

where K is a constant, $M(\overline{Rg}.i)$ is the mass fraction of the particles with radius of gyration $\overline{Rg}.i$, and h is $4\sin\theta/\lambda$,λ being the wave-length. When the shape of the particle is spherical, the relation between the particle's diameter D and the $\overline{Rg}$ is as follows:

$$\overline{Rg}^2 = \frac{3}{20}D^2 \qquad (2)$$

Porod (1951, 1952), based on Debye's theory, elaborated a general theory of X-ray scattering which is applicable to the small-angle scattering of colloidal systems. According to this theory, the scattering integration is as follows:

$$I(h) = Ie(h) \cdot V \cdot \rho^2 (1 - \omega)\omega \int_0^\infty H(r) \frac{\sin hr}{hr} 4\pi r^2 \cdot dr \tag{3}$$

where $Ie(h)$ is the intensity of X rays scattered by one electron, V is the total volume of the specimen irradiated, ρ is the mean electron density in the particles, ω is the packing density of the specimen, and $H(r)$ is the characteristic function of the specimen. From Eq. (3), Porod introduced several useful parameters. One of them is designated as the "extent of coherence" and is defined as

$$\begin{aligned} lc &= 2 \cdot \int_0^\infty H(r) \cdot dr \\ &= \pi \int_0^\infty h \cdot I(h) \cdot dh \Big/ \int_0^\infty h^2 \cdot I(h) \cdot dh \end{aligned} \tag{4}$$

The value of lc represents the average length of all the diameters of a particle, which are measured through every point in the particle. When the shape of the particle is spherical, the relation between the particle's diameter D and the lc is as follows:

$$lc = 3/4D \tag{5}$$

Another important parameter is the "structure-index," f, which is defined as follows, assuming that the value of $h^4 \cdot I(h)$ is constant in the higher angle region:

$$f = \left[\lim_{h \to \infty} h^4 \cdot I(h) \right] \cdot \int_0^\infty h \cdot I(h) \cdot dh \Big/ \left(\int_0^\infty h^2 \cdot I(h) \cdot dh \right)^2 \tag{6}$$

According to Eq. (6), the value of f is 1/2, when the sample consists of identical spherules. Heterogeneity of particles in shape and size causes the value of f to be larger than 1. A large f-value, such as 3–4, is seen in platy or fibrous particles even when their sizes are uniform. Therefore, the f-value indicates the shape of the particle.

Adopting these theories, the radius of gyration $\overline{Rg}$ and the "extent of coherence" lc would be reasonably estimated, regardless of particle shape. Porod's theory for interpreting the small-angle scattering includes only an assumption that all particles have a homogeneous electron-density. In the Jellinek-Solomon-Fankuchen theory, the inter-particle interference is usually neglected.

The purpose of this paper is to apply Jellinek-Solomon-Fankuchen's and Porod's theories to the measurement of the particle size of clay minerals.

Materials

It was made sure that the samples examined in this study contained no other materials, by means of X-ray diffraction and differential thermal analysis. Existence of other materials, if any, was stated clearly. The clay minerals investigated in this study were kaolinite, hydrated halloysite and allophane.

Kaolinite: Kanpaku, Tochigi Prefecture

Very large euhedral flakes up to 60,000 Å in diameter with a lesser amount of fine materials and elongated particles were distinguished in the electron micrograph. The sample was shown to be free from impurities by X-ray powder analysis and DTA.

Hydrated halloysite: Inage, Chiba Prefecture

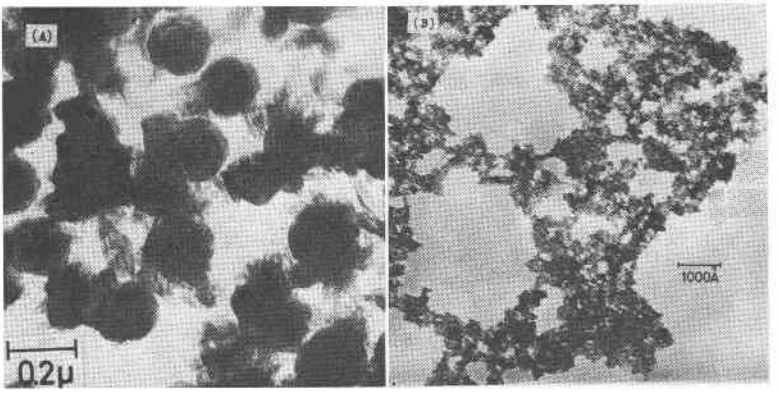

Fig. 1. Electron micrographs. A: hydrated halloysite, B: allophane.

This sample was taken from the weathering crust of volcanic ash. Its electron micrograph shows an aggregate of spherical particles (Fig. 1A.) Such spherules have been reported in Japan in many papers (Sudo and Takahashi, 1956), and it has been agreed that they are usually a product in an intermediate process of transformation of allophane into halloysite, and that it is actually composed of extremely fine halloysite and allophane particles. Although the present material shows X-ray diffraction of hydrated halloysite only, allophane is probably in the sample. The writer's present data is conerned with the bulk result obtained from this sample. The detailed analysis concerning the effects due to allophane or hydrated halloysite will be reported elsewhere.

Allophane: Kanuma, Tochigi Prefecture

The allophane sample was collected from the so-called "Kanuma-soil." It is composed of pumice fragments that have completely altered to allophane, and a gel-like material filling interspaces of these altered pumice fragments. In distilled water, the gel-like substance was gathered by hand-picking. The pumice without gel-like substance was disintegrated by dispersing it in water of pH 4. Adding 1N NaOH, the floating matter was decanted, and allophane gathered.

Allophane shows a few broad X-ray bands of 12.6 Å, 3.4 Å and 2.3 Å. After heating at

300°C for 30 hrs., these powder reflections are weakened except one broad halo at about 5-3.3 Å.

The differential thermal curve of allophane shows an endothermic peak at about 140°C and exothermic peaks at about 920°C and 944°C. The value of SiO_2/Al_2O_3 was 1.37. Electron micrograph shows that this allophane consists of very fine spherical particles (Fig. 1B). The properties of gel-like material have been already reported by Kanno *et al.*, (1960), and agree with those of "imogolite" (Wada (1967)). Mineralogical data for the gel substance will be reported at a later date.

Experiments

The instrument used for measuring small-angle X-ray diffraction from clay-particles is the C-1 type made by the Rigakudenki Co. Fig. 2 shows the slit system of the apparatus. O_1 and O_2 are slits, and the length of v, w and s is variable. The slits are rectangular: 0.5, 0.3, 0.2, 0.1, 0.05 mm in width, and 10 mm in height. The condition for selecting the slit and the length of v, w, and s will be stated in the following section.

The scattering intensity was measured by Geiger counter on the observation plane under the condition where a linear relation is assumed between the scattering energy of X-ray and the observed intensity.

In order to cut down the scattering by air a vacuum can was set between the sample and the observation plane.

The X-ray source was a Cu-target tube operated at 30 KV and 15 mA, and Cu·Kα(λ =1.542 Å) radiation monochromatized by the double-filter method of Ross (1926, 1928). The balanced filters are made of nickel and cobalt foil available on the market.

The measurement of the small-angle scattering was carried out under an experimental condition where the error due to the beam width can be avoided. According to Kuroda (1956), the experimental condition for Cu·Kα radiation is as follows:

$$\begin{aligned} \overline{Rg}\cdot_{max} &< 0.2\, s/A \text{ (Å)} \\ \overline{Rg}\cdot_{min} &> 1.6\, s/B \text{ (Å)} \end{aligned} \tag{7}$$

where s is the length between the sample and the observation plane, A and B are the width and the height of incidental X-ray on the observation plane, $\overline{Rg}\cdot max.$ and $\overline{Rg}\cdot min.$ are the maximum and the minimum of the radius of gyration in the assemblage of the particle. In this study, the slit was selected under the condition shown in Eq. (7). The length of w, v and s is fixed as; $v=s=275$ mm, $w=35$ mm. The slit system and $\overline{Rg}\cdot max.$ are as listed below.

No. of slit system	1st slit (O_1)	2nd slit (O_2)	$\overline{Rg}\cdot$max.
(1)	0.5×10 mm	0.3×10 mm	53 Å
(2)	0.3×10	0.2×10	83
(3)	0.2×10	0.1×10	144
(4)	0.1×10	0.05×10	275

The scattering intensity was registered by the fixed-count measurements. Several intensity curves were drawn for each specimen, with various slit systems. A series of intensity curves for each specimen were combined by graphical matching to get a complete scattering curve extending from 8′ to 70′ of the scattering angle. The result for kaolinite is shown in Figure 3.

In this study, the incident beam can be considered infinitely high even for the most distant part of the intensity curve. Using the observed intensity $i(h)$, Porod (1953) and

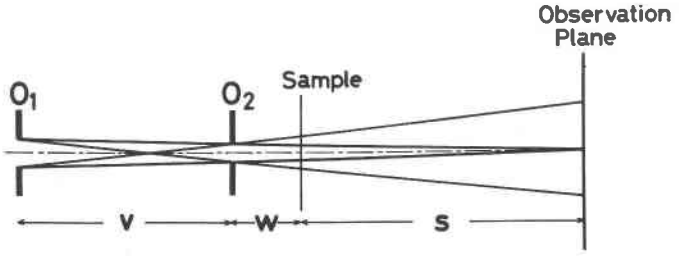

FIG. 2. Slit collimation system. O_1: 1st slit, O_2: 2nd slit.

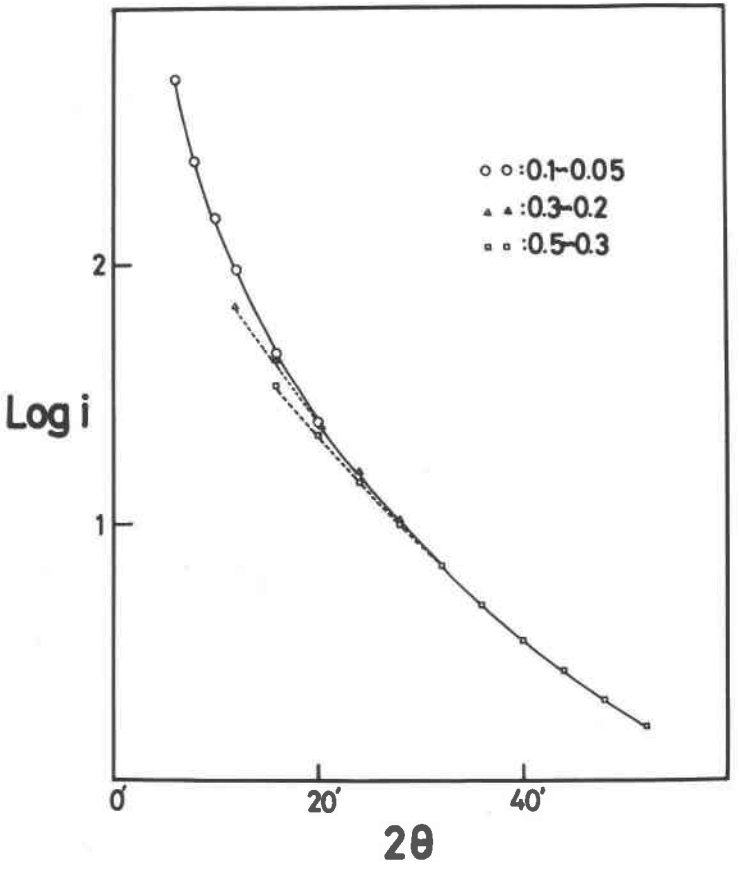

FIG. 3. A series of intensity curves for kaolinite. ○: slit system No. 1; Δ: slit system No. 3; □: slit system No. 4.

Kakudo (1957) derived the following equations from equations (1), (4) and (6):

$$i(h) = K' \sum_{i} M(\overline{Rg}\cdot i)\cdot(\overline{Rg}\cdot i)^2\cdot\exp(-h^2\cdot(\overline{Rg}\cdot i)^2/3)$$
$$lc = 2\cdot\int_0^\infty i(h)\cdot dh \Big/ \int_0^\infty h\cdot i(h)\cdot dh \qquad (8)$$
$$f = [\lim_{h\to\infty} h^3\cdot i(h)]\cdot\int_0^\infty i(h)\cdot dh \Big/ \int_0^\infty h\cdot i(h)\cdot dh^2,$$

where K' is constant.

Graphical analysis of the curve of $i(h)$ was made in order to evaluate $M(\overline{Rg}\cdot i)$, lc and f. (Fig. 4, 5).

Results and Discussion

General.

Table 1. Radius of Gyration, Coherence, and Structure Index

Sample	$\langle\overline{Rg}\rangle$	lc	f
Kaolinite	153 Å	468 Å	1.5
Hydrated halloysite			
unheated sample	141	334	1.1
heated sample	120	267	1.3
Allophane			
original sample	39	—	—
ground sample	145	411	2.7
further ground sample	181	472	1.8
heated sample	45	—	—

The particle size of clay minerals was measured by the method mentioned above in the region below 275 Å in radius of gyration.

The graph of log $i(h)$ versus $(2\theta)^2$ showed no linear part for any of the clay samples (Fig. 4). This means that the particles of clay minerals are not uniform in size. Therefore, the mass fraction of the particles, $M(\overline{Rg})$ and the average value of radius of gyration $\langle\overline{Rg}\rangle$ were obtained by Jellinek-Solomon-Fankuchen's method.

The "extent of coherence" lc and the "structure-index" f were calculated by the intergrations in equation (8). The values of lc and f of raw allophane and allophane heated to 300°C could not be calculated.

The results are given in Table 1 and Figure 6.

Kaolinite and hydrated halloysite. The powdered dry kaolinite gave an average radius of gyration as 153 Å and the value of lc as 468 Å. For hydrated halloysite, the values of $\langle\overline{Rg}\rangle$ and lc were 141 Å and 334 Å. For kaolinite and hydrated halloysite, the value of f (=1.45 or 1.1) showed that the particle shape was not platy, and the value of $M(\overline{Rg})$ increased with the increasing radius of gyration (Fig. 6A).

Judging from these data, the particle size of these samples would be larger than 275 Å in radius of gyration, and it seems probable that such large flakes would contribute very little to the small-angle scattering in the range below 275 Å in radius of gyration, and that the results obtained are a measure of the finer material with a contribution from the thickness of the large flakes or allophane included in "halloysite-allophane spherule."

Effect of heat treatment for hydrated halloysite. Hydrated halloysite was heated at 110°C for one hour. Comparing between hydrated halloysite

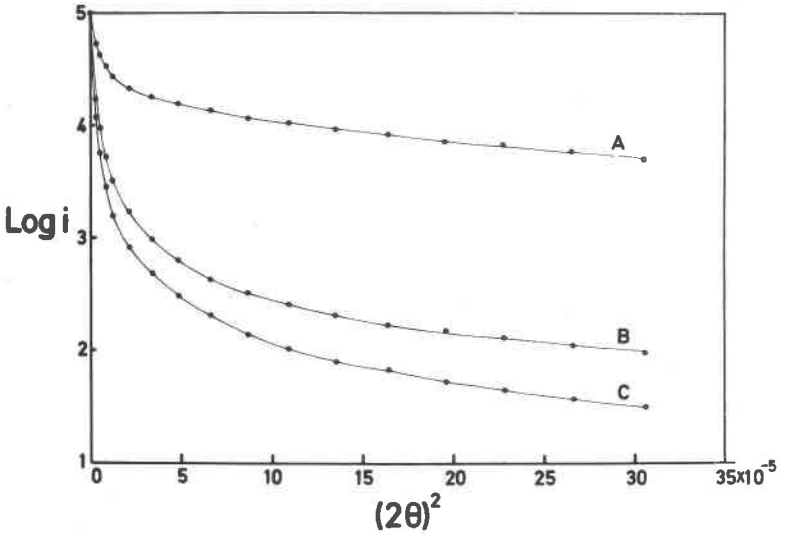

FIG. 4. The graph of log $i(h)$ versus $(2\theta)^2$ for clay minerals. A: allophane, B: hydrated halloysite, C: kaolinite.

and heated hydrated halloysite, $\langle\overline{Rg}\rangle$ and lc of hydrated halloysite were smaller than those of the heated specimen. From evaluation of f, the particles of heated hydrated halloysite were less uniform than those of raw hydrated halloysite. After heat treatment, the value of $M(\overline{Rg})$ of larger particles than 275 Å in radius of gyration became smaller. This fact shows that the particle size of hydrated halloysite was related to dehydration due to heated treatment (Fig. 6B).

Allophane. The particles of dry powdered allophane were examined. By Jellinek-Solomon-Fankuchen's method, the largest value of $M(\overline{Rg})$ occurred at the smallest radius of gyration (Fig. 6A). However, the value of

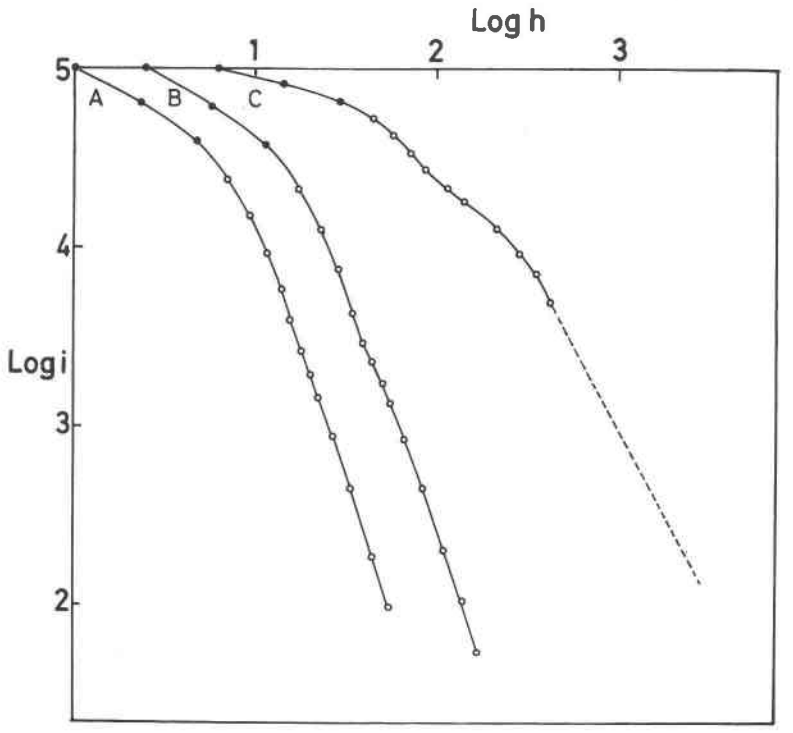

FIG. 5. The graph of log $i(h)$ versus log h for clay minerals. A: kaolinite, B: hydrated halloysite, C: allophane. ○: observed; ●: extrapolated mathematically, broken line: extrapolated graphically.

lc or f of this sample was not obtained, because the value of $\lim_{h\to\infty} h^3.i(h)$ was inconstant (Fig. 5). A phenomenon like this has been reported in the case of silica-gel and alumina-gel by Porod (1953).

The value of $\overline{Rg}$ which gives the largest value of $M(\overline{Rg})$ is below 275 Å. When the shape of the particle is spherical, the value of D by Eq. (2) is about 100 Å, which agrees with the diameter obtained from electron micrograph (Fig. 1B).

Effect of grinding. Dry powdered allophane was ground in an agate mortar at room temperature for a few minutes. After the grinding treatment, the values of $\langle\overline{Rg}\rangle$ and lc increased. Further grinding gave the larger value of $\langle\overline{Rg}\rangle$ and lc, but the smaller value of f. The present result indicates that after the grinding treatment the particles which are responsible for the scattering became larger and more identical in size.

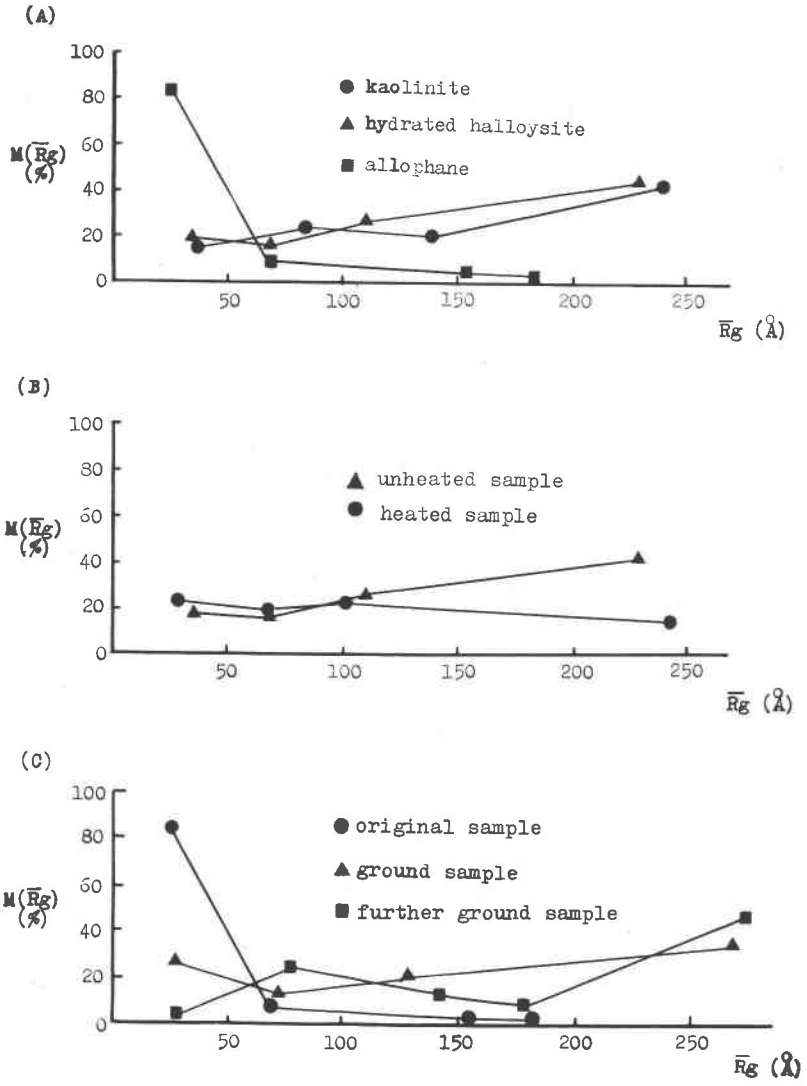

FIG. 6. Distribution of the radius of gyration. A: clay minerals used in this study, B: hydrated halloysite after heat treatment, C: allophane after grinding treatment.

Effect of heat-treatment on allophane. The raw allophane was heated up to 300°C for 20 hrs. After the heating, the small-angle scattering remained almost unchanged, whereas the X-ray powder pattern changed.

These data indicate that the two theories for the small-angle scattering

are generally applicable to clay minerals with the limit of $\overline{Rg}$ determined from equation (7). At first the condition of slit is examined and the exact size and distribution of clay particle size should be calculated with the aid of Jellinek-Solomon-Fankuchen's and Porod's method.

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