

## SIZE DISTRIBUTION OF ALLOPHANE UNIT PARTICLES IN AQUEOUS SUSPENSIONS

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**Abstract**—The size distribution of unit particles of two New Zealand allophanes (An and Rh), in dilute (0.8% w/v) aqueous suspensions, has been determined by small-angle neutron scattering (SANS). In addition, the specific surface area of the samples was measured by ethylene glycol retention, and their morphology examined by high-resolution transmission electron microscopy (HRTEM). The SANS data indicate that although both allophanes are somewhat polydisperse, the average diameter of their unit particles is significantly different, being 56 and 43 Å for allophane-An and allophane-Rh, respectively. Consistent with this observation, the specific surface area of allophane-Rh (897 m<sup>2</sup>/g) is appreciably greater than that of allophane-An (638 m<sup>2</sup>/g). Under the electron microscope, both samples appear as aggregates of hollow spherules but HRTEM did not clearly distinguish between the two allophanes in that the largest population of spherules had diameters near 50 Å. Because of the assumptions and uncertainties involved in the SANS and surface area measurements, the data must be discussed in terms of their respective ratios. On this basis, the spherule diameter ratio is of the same order of magnitude as the inverse ratio of specific surface area. The latter value is also in reasonably good agreement with the corresponding ratios of phosphate adsorption capacity and BET nitrogen areas, derived from earlier studies.

**Key Words**—Allophane, High-resolution transmission electron microscopy, Morphology, Particle size, Small-angle neutron scattering, Surface area.

### INTRODUCTION

Allophanes have been shown to vary in their charge characteristics, phosphate-sorption capacity, pore-size distribution, and specific surface area (Kitagawa, 1971; Egashira and Aomine, 1974; Paterson, 1977; Vandickelen *et al.*, 1980; Theng *et al.*, 1982). Although these observations have been explained in terms of variations in chemical composition, defect structures, and interparticle arrangement among samples, it seems probable that the relative size of the allophane unit particles is a contributing factor. In support of this view, high-resolution electron microscopy (HRTEM) has indicated that these units are hollow spherules with an external diameter ranging from 35 to 55 Å and a wall thickness of 7–10 Å (Wada and Wada, 1977; Wada, 1979). Electron micrographs of allophane, however, require rapid exposures because thermal dehydration in the electron beam may lead to an irreversible collapse of the spherules (Henmi and Wada, 1976). This possibility does not arise when the size distribution of colloidal particles is measured in dilute suspension using either small-angle X-ray or neutron scattering. The

former method has been applied by Watanabe (1968) and Watanabe and Sudo (1969) to allophane, but in using relatively dry samples, their data may have been influenced by interparticle interferences.

Here we report on the application of small-angle neutron scattering (SANS) as a quantitative, non-destructive technique for determining the particle-size distribution of allophane in aqueous dispersions as exemplified by the work of Cebula *et al.* (1980) on montmorillonite sols. The data obtained by this means are compared with those derived from surface area and electron optical measurements.

### MATERIALS AND METHODS

Two New Zealand allophanes of differing composition, origin, and age were used. Allophane-An with a molar Al/Si ratio of 1.95 was derived from andesitic ash produced by the eruption of Mt. Egmont 6000 years ago. The other sample, allophane-Rh, has an Al/Si ratio of 1.57 and originated from the rhyolitic Rotoehu tephra deposit, dated at 42,000 years B.P. The <2- $\mu$ m e.s.d. fraction of each sample was obtained by dispersing the bulk material at pH 3.5 with an ultrasonic probe, sedimenting it under gravity, coagulating it with 1 M NaCl solution, and removing excess salt by repeated washing with distilled water. A full description

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of the sample localities, together with details of the infrared spectra and other surface properties of the samples, have been given elsewhere (Parfitt and Henmi, 1980; Theng *et al.*, 1982).

The SANS measurements were carried out with the spectrometer in the PLUTO reactor at the Atomic Energy Research Establishment (AERE) in Harwell, United Kingdom. This instrument is of similar design to earlier models developed elsewhere (Schmatz *et al.*, 1974) and incorporates a helically slotted rotating drum which provides monochromation and an evacuable sample chamber. The two-dimensional, position-sensitive BF<sub>3</sub> detector of the LETI type gave a resolution element of 0.5 cm by 0.5 cm with a scattered-neutron flight path of 2.1 m. The allophane samples were introduced as a 0.8% w/v aqueous (100% H<sub>2</sub>O) suspension of 1 mm thickness, contained in "Spectrasil" cells with 1-mm thick walls. All measurements were made at ambient temperature and an incident neutron wavelength of 6 Å. The neutron beam at the sample position had a circular cross-section of 8 mm.

The specific surface area of the allophane samples was determined by the ethylene glycol (EG) retention method of Dyal and Hendricks (1950) as modified by Bower and Goertzen (1959). Weighed amounts (~0.3 g) of the air-dry clays, contained in weighing bottles, were dried over P<sub>2</sub>O<sub>5</sub> in an evacuable desiccator at room temperature. The dried samples were covered with liquid EG (~2 cm<sup>3</sup>) and placed in a desiccator over a CaCl<sub>2</sub>-EG solvate overnight. The desiccator was then evacuated using a rotary pump until the excess (free) liquid had visibly disappeared. The bottles were weighed and the evacuation procedure continued until constant weight was attained. At this point the quantity of EG retained was assumed to correspond to that required for a monolayer coverage of the accessible surface.

The high-resolution transmission electron micrographs at a magnification of 50,000× were obtained from the allophane suspensions dried on a plastic microgrid with 1–5-μm size perforations (Fukami and Adachi, 1965). The samples were examined using a JEM 100B instrument at an accelerating voltage of 100 kV (Henmi and Wada, 1976).

## RESULTS AND DISCUSSION

### *Small-angle neutron scattering measurements*

Inasmuch as both allophane samples exhibited radially symmetric scattering, the initial data reduction consisted of radial summation and subtraction of the background due to scattering from the cell. The corrected data are shown in Figure 1 as plots of scattered intensity against  $Q$ , where  $Q$  is the magnitude of the scattering vector and  $hQ/2\pi$  is the momentum transferred in the scattering event. For elastic scattering

$$Q = 4\pi \sin(\theta/2)/\lambda, \quad (1)$$

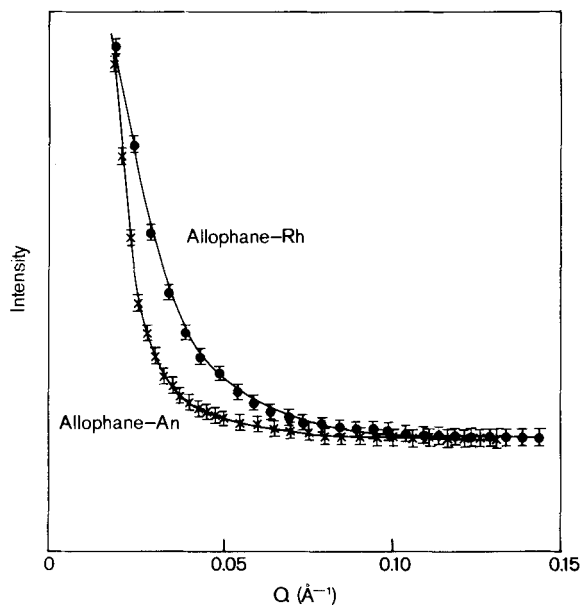


Figure 1. Small-angle neutron scattering from 0.8% w/v aqueous (100% H<sub>2</sub>O) suspensions of allophane-Rh and allophane-An. The solid curves are theoretical profiles for the best-fit distribution functions illustrated in Figure 2. The intensity scale is linear.

where  $\theta$  is the scattering angle and  $\lambda$  the neutron wavelength.  $Q$  is inversely proportional to the inhomogeneity dimension sampled by the measurement. For  $\lambda = 6$  Å on the AERE Harwell instrument the observable particle size ranges from 20 to 350 Å. Figure 2 shows that the size distribution of allophane-An is significantly different than that of allophane-Rh.

A simple analysis of the data using the Guinier approximation (Guinier and Fournet, 1955), utilizing the equation

$$I(Q) = \exp(-Q^2 R_g^2/3), \quad (2)$$

where  $R_g$  is the radius of gyration of the scattering particle, further suggests that both samples are somewhat polydisperse. Thus, a plot of  $\log(I)$  against  $Q^2$  shows no well-defined region of linearity, even at low values of  $Q$ . For polydisperse systems, the  $R_g$  values derived from Eq. (2) do not correspond to the mean or most probable sizes; rather, they are heavily biased towards the largest observable particle sizes because the magnitude of  $I$  for individual particles is weighted by the square of the particle volume (Guinier and Fournet, 1955). For this reason, the data were analyzed on the basis of a model comprising a finite distribution of spherical particles having discrete radii,  $R_k$ .

Assuming that the suspended particles and the aqueous medium have constant scattering length densities of  $\rho_a$  and  $\rho_w$ , respectively, and ignoring interparticle interferences, the coherent scattering cross-section per atom is given by the expression

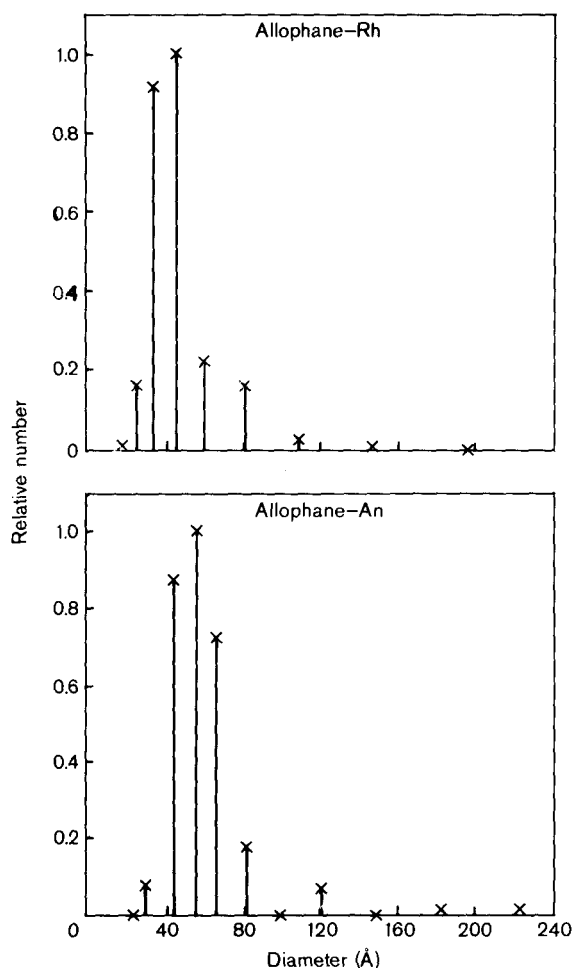


Figure 2. Fitted unit particle-size (diameter) distribution functions for allophane-Rh and allophane-An.

$$\frac{d\sigma}{d\Omega}(Q) = \frac{1}{N} \sum_k n_k V_k^2 (\rho_a - \rho_w)^2 |F_k(Q)|^2. \quad (3)$$

Here,  $N$  is the total number of atoms,  $n_k$  is the number of particles of radius  $R_k$ , and  $V_k = 4\pi R_k^3/3$ ;  $F_k(Q)$  is the single-particle form factor, which for spheres is given by the Rayleigh expression

$$F_k(Q) = 3 \{ [\sin(QR_k)] - QR_k \cos(QR_k) \} / (QR_k)^3 \quad (4)$$

(Kostorz, 1979). The predicted scattering profile consists of a term proportional to the coherent small-angle scattering cross-section, plus a constant background from isotropic incoherent scattering, principally due to the water protons. The particle-size distributions, defined by the values of  $n_k$ , were calculated using the constrained least-squares fitting method of Vonk (1976).

Figure 2 illustrates the diameter distribution functions for the two allophanes, the fitted scattering profiles being represented by the solid curves in Figure 1.

The histograms were calculated in equal intervals of  $\log(\text{diameter})$ . The calculated distribution for allophane-An tends towards larger diameters than that for allophane-Rh, averaging 56 Å as compared to 43 Å.

The walls of allophane spherules apparently contain defect structures or "pores" of  $\sim 3$  Å diameter which permit water molecules to enter and occupy the (hollow) interiors of the unit particles (Henmi and Wada, 1976). If this reaction had occurred, contrast would have been lost (in the SANS experiment) between the interior and the bulk liquid phase. The single-particle form factor should then perhaps have been modified to that appropriate for spherical shells having external and internal radii of  $R_2$  and  $R_1$ , respectively, as follows:

$$F(Q) = [f(QR_2) - f(QR_1)]/Q^3(R_2^3 - R_1^3), \quad (5)$$

where

$$f(QR) = 3[\sin(QR) - QR \cos(QR)]. \quad (6)$$

The difference between the values of  $R_2$  and  $R_1$  represents the thickness of the spherule wall which is in the range 7–10 Å (Wada, 1979). Unfortunately, this specific model was not easily incorporated into the FORTRAN program used to analyze the data, mainly because the program contained a limited number of geometrical options including those appropriate to spheres and shells of negligible wall thickness (Vonk, 1976). Cross-section calculations of particle-size distributions like those illustrated in Figure 2, however, were performed for all three models, i.e., solid spheres and shells with either a finite or a negligible wall thickness. The results indicate that the solid-sphere option is a good representation for allophanes if most of the interior volume is empty. If, on the other hand, most of this volume is filled with water, use of the solid-sphere model may lead to an overestimate of particle diameters by 5–10%. Nevertheless, such a model is more reliable than one in which the wall thickness of the shell is negligible as compared to its diameter. A hollow sphere model might have provided a further refinement; however, because of uncertainties regarding the value to be used for the wall thickness and the extent to which the interior of the spheres is filled with water, such a treatment did not appear to be justified.

#### Surface areas

Specific surface areas ( $S$ ) were calculated by taking a value of 30 m<sup>2</sup>/g for each 1% w/w of EG retained at monolayer coverage, giving a cross-sectional area of 30.88 Å per molecule (Brindley, 1966). On this basis and assuming no penetration of the interior spherule space by the organic liquid,  $S$  values of  $638 \pm 25$  and  $897 \pm 38$  m<sup>2</sup>/g were obtained for allophane-An and allophane-Rh, respectively. The cross-sectional area used was an average, derived from retention measurements on montmorillonite of essentially planar surface geometry (Theng, 1974). For curved surfaces with a

small radius of curvature, as for the present materials, the area occupied by each EG molecule is larger than in montmorillonite (Paterson, 1977). If anything, the *S* values quoted above underestimated the extent of the external spherule area.

For spherical particles, *S* may also be calculated using the relationship

$$S = 6/\rho D \times 10^4, \quad (7)$$

where  $\rho$  is the specific gravity or density (in g/cm<sup>3</sup>) and *D* is the diameter (in Ångstrom units). Taking  $\rho = 2.6$  for allophane (Wada, 1980) and inserting the experimentally determined *S* values in Eq. (7), diameters of 36 and 26 Å for allophane-An and allophane-Rh, respectively were calculated. These values are 35–40% smaller than the corresponding diameters determined by SANS.

#### Electron microscopy

The electron micrographs (Figure 3) show that both allophanes consist of porous aggregates of varying size and shape. Each aggregate, in turn, is made up of hollow spherules with external diameters of 40–55 Å, the largest relative population having diameters near 50 Å. The similarity in unit particle shape and size between allophanes of different age, composition, and origin has also been noted by Kitagawa (1971), Henmi and Wada (1976), and Wada and Wada (1977). HRTEM is clearly not well suited for distinguishing between allophane samples with respect to their particle-size distribution because of spherule aggregation and possible collapse during sample preparation and examination.

#### Data comparison

Figure 2 indicates that the unit particles of allophane-An are, on average, appreciably larger than those of allophane-Rh. This observation is based on a model of homogeneous, solid spheres with a discrete distribution of radii, analyzed using equations appropriate for a single scattering system of suspended particles. In reality, however, the particles are hollow spherules (Figure 3), and multiple scattering between such particles and the suspending medium (water) should have occurred during the experiment. In view of the assumptions involved, the average spherule diameters derived from SANS measurements should be regarded as relative values. By the same token, the EG-retention method is more suited for comparative than for absolute determinations of specific surface areas (Theng, 1974).

For these reasons, the data obtained from different sets of measurements are best compared in terms of their respective ratios. Thus, the ratio of average spherule diameters ( $D_{An}/D_{Rh}$ ) derived from SANS is 1.30. Inasmuch as  $D \propto 1/S$  (Eq. (7)), this value should be compared with the inverse specific-surface-area ratio ( $S_{Rh}/S_{An}$ ) of 1.40, obtained from EG retention. The

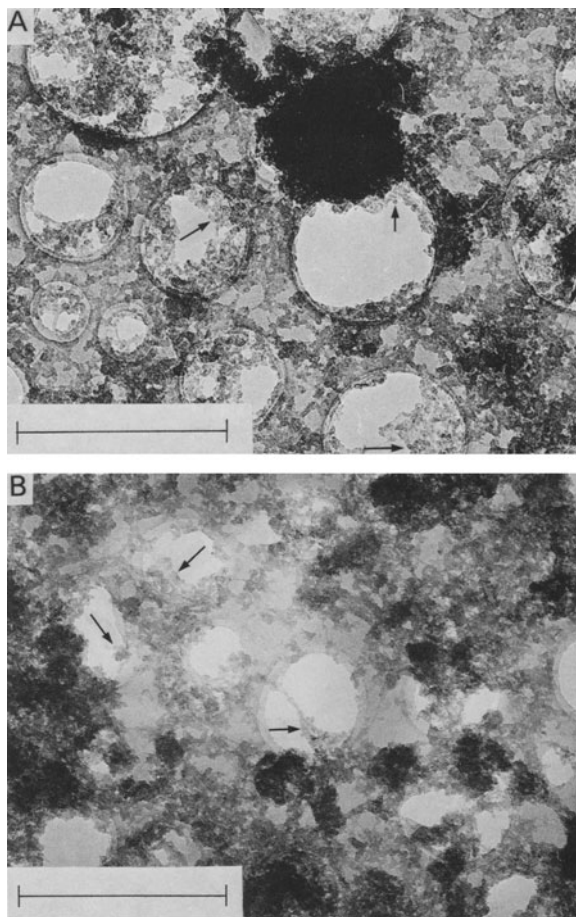


Figure 3. High-resolution transmission electron micrographs of (A) allophane-Rh, and (B) allophane-An. Arrows indicate well-resolved aggregates of unit particles. Length of bar represents 0.5  $\mu\text{m}$ .

good agreement between these two sets of data indicates that the specific surface area of allophanes, which can readily be determined, may serve as an index of their respective spherule size. It is also interesting to note in this context that the ratio of phosphate adsorption capacity, taken at a point where the isotherms begin to level off, is of the same order of magnitude (Theng *et al.*, 1982).

Earlier, Vandickelen *et al.* (1980) independently derived BET specific surface areas and pore-size distributions for allophane-Rh ("waxy-pan") and allophane-An ("Egmont") from their respective adsorption-desorption isotherms of  $\text{N}_2$  at  $-195^\circ\text{C}$ . They obtained a  $S_{Rh}/S_{An}$  ratio of 1.73 for samples which had previously been outgassed at  $\sim 200^\circ\text{C}$ , a treatment comparable to that used for HRTEM examination which should also have involved a strong heating effect. Although showing the same trend, this value is 20% larger than the corresponding ratio determined by EG retention. Their pore-size distribution data indicate,

however, that allophane-Rh has a relatively large volume of pores in the 30–50 Å radius range which are accessible to N<sub>2</sub>. These pores may be identified with interspherule spaces because nitrogen appears to be incapable of penetrating the spherule interiors (Pater-son, 1977). Although the electron micrographs (Figure 3) are again inconclusive on this point, they suggest that the interspherule pores in allophane-Rh occupy a larger volume than those in allophane-An.

### CONCLUSIONS

High-resolution transmission electron microscopy has shown that the unit particles of allophanes invariably consist of hollow spherules with external diameters of 35–50 Å, irrespective of the age, composition, and origin of the samples. The variation in spherule size has been confirmed here by small-angle neutron scattering (SANS) on dilute aqueous suspensions, thus avoiding the possibility of spherule collapse during evacuation and through heating under the electron beam. The SANS data are also consistent with specific surface area and phosphate-adsorption measurements in that the ratio of average spherule diameter of the samples is of the same order of magnitude as their inverse ratios of surface area and phosphate-adsorption capacity. The variation in particle-size distribution, however, needs to be further tested on a wider range of allophanes, and by using different colloid chemical techniques, such as X-ray scattering. In particular, SANS studies on samples suspended in H<sub>2</sub>O-D<sub>2</sub>O mixtures of varying composition would provide variable contrast between the components of the system. The results would shed further light on the degree of polydispersity and the extent to which the spherule interiors are filled with the suspending liquid. Although the SANS method is experimentally straightforward and clearly of great potential for studying clay-water systems (Ross and Hall, 1980), the restricted access to spectrometers and ancillary facilities makes for difficulties in its application on a routine basis.

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