MEASUREMENT OF THICKNESS OF DISPERSED CLAY FLAKES WITH THE ELECTRON MICROSCOPE

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ABSTRACT

The shadow lengths of dispersed flakes of the layer-lattice mineral, allevardite, were measured with the electron microscope. Details of the experimental technique are given, and the importance of using samples free from very small material is stressed. Measurements of flake thickness made in this way agree well with estimates of the basal spacing of the collapsed lattice obtained from X-ray diffraction, and dispersion of allevardite was found to produce suspended flakes 19 Å thick, corresponding in thickness to the basic structural unit of two 2:1 layers.

INTRODUCTION

Dispersion of sodium-saturated montmorillonites produces extremely thin flakes or laths, and it has been suggested that these flakes have a thickness of only one or two structural units (Ross and Hendricks, 1945; Grim, 1953, p. 116; Bates, 1958). Allevardite, another expanding layer-lattice clay mineral, also disperses into extremely thin flakes. It differs from montmorillonite in that the basic structural unit consists of double rather than single 2:1 layers, and shows montmorillonitelike interlayer swelling between adjacent double layers. Brindley (1956) showed that swelling of this kind in the allevardite from Allevard can be explained by assuming that alternate interfaces of the 2:1 units have charge densities similar to those of a low-charge-density mica, $0.7/Si_4O_{10}$, and pyrophyllite, $0.0/Si_4O_{10}$, respectively, and that interlayer swelling takes place at the interfaces with zero charge density.

Allevardite was selected for studies on measuring flake thickness by electron microscopy because we had samples exceptionally free from fine-grained contaminating material, and because the flakes, being thicker than those of sodium-saturated montmorillonites, were more easily measured.

DETAILS OF THE SPECIMENS

The three mineral samples used had similar chemical analyses and X-ray diffraction characteristics and will be referred to as allevardites after the La Table mineral.

(1) Locality: La Table near Allevard, Savoie, France. Designation: A-allevardite (Plate 1, a). References: Caillère, Mathieu-Sicaud and Hénin (1950), Hénin, Esquevin and Caillère (1954), Brindley (1956).

(2) Locality: near Brunjkaki, Fort Sandeman district, Baluchistan, Pakistan. Designation: B-allevardite (Plate 1, b). This specimen was obtained from the Pakistan Geological Survey via the British Museum and is very similar in chemical-structural composition to the La Table specimen.

(3) Locality: Dagestan, U.S.S.R. Designation: D-allevardite (Plate 2, a). Reference: Ivkin *et al.* (1959), who identified it as an allevardite by direct comparison with the La Table mineral.

EXPERIMENTAL TECHNIQUE

The allevardites were dispersed by shaking in solutions of sodium hexametaphosphate or sodium chloride, and freed from excess salt by repeated sedimentation in the centrifuge followed by resuspension in double-distilled water. Samples for electron microscopy were diluted with double-distilled water and sprayed onto freshly cleaved mica surfaces with an "Aerograph" air brush (Nixon and Fisher, 1958).

The mica flakes bearing the dried droplet traces were then placed in an evaporating plant and shadowed with platinum or platinum–iridium at an angle of about 11°. Preliminary experiments indicated that shadows cast at this angle yield mounts showing a satisfactory compromise between adequate shadow length and the very large increase in granularity which results from shadowing at low angles. The evaporator was equipped with a collimating system of two apertures between the filament and specimen so that only metal from the tip of the V-shaped filament could fall on the specimen. The shadowing angle was calculated for each evaporation from the measured positions of the filament tip and the center of each mica flake. While in the evaporator the mica flakes tended to curl slightly at the edges, but errors in the angle of shadowing arising from this were avoided by taking specimens only from the center of the flakes. The usual method of estimating the shadow angle by including polystyrene Latex in the sample and calculating the local shadow angle from the known diameter of the Latex particles is unsatisfactory because the Latex particles are thermoplastic and tend to flatten in the radiant heat from the evaporator filament. This effect is particularly serious with the high filament temperatures needed to evaporate platinum and its alloys.

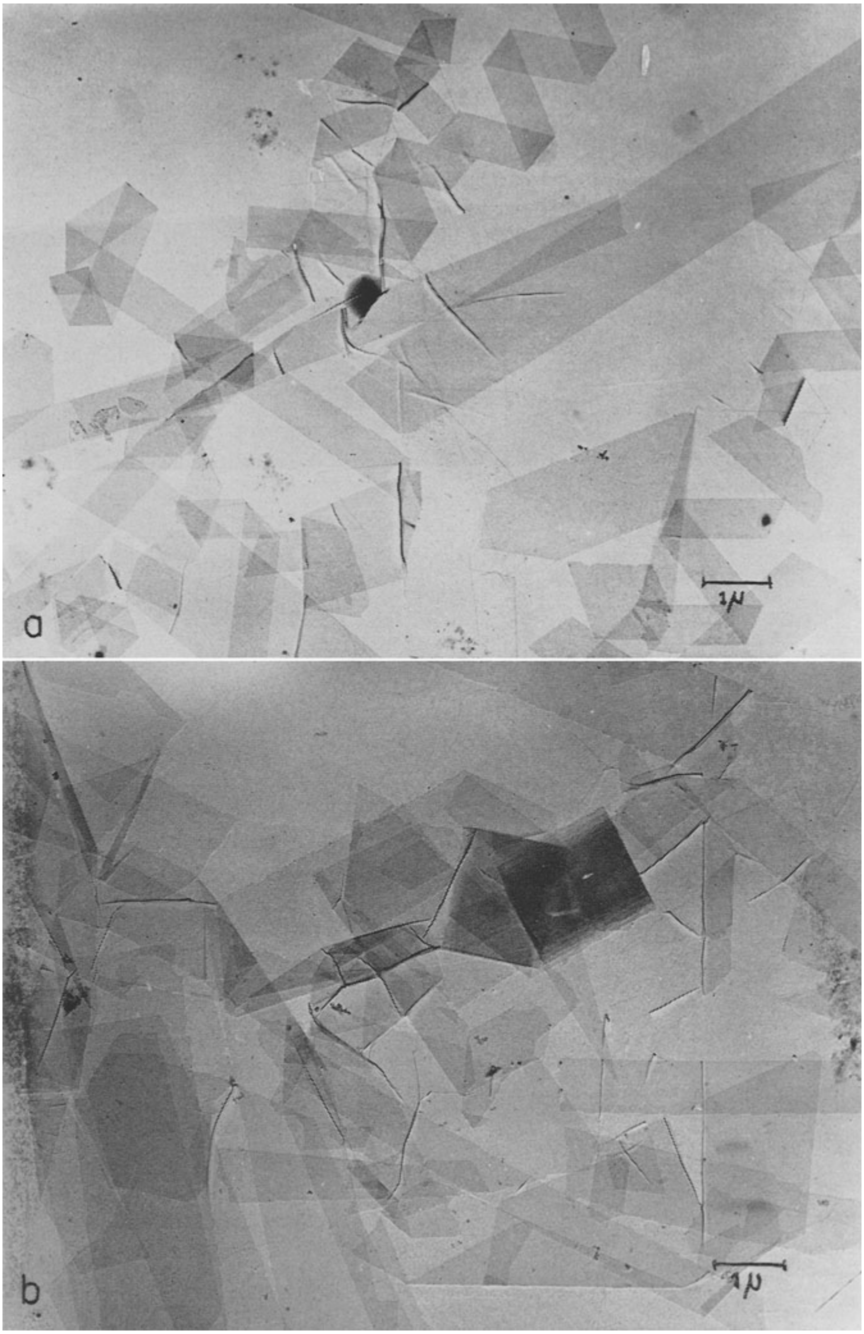

Plate 1.—(a) Electron micrograph of A-allevardite, mounted as described in the text. 8200 ×. (b) Electron micrograph of B-allevardite, mounted as described in the text. 8200 ×.

Technical data: Platinum–iridium shadowing, cast at an angle of 11°, positive prints.

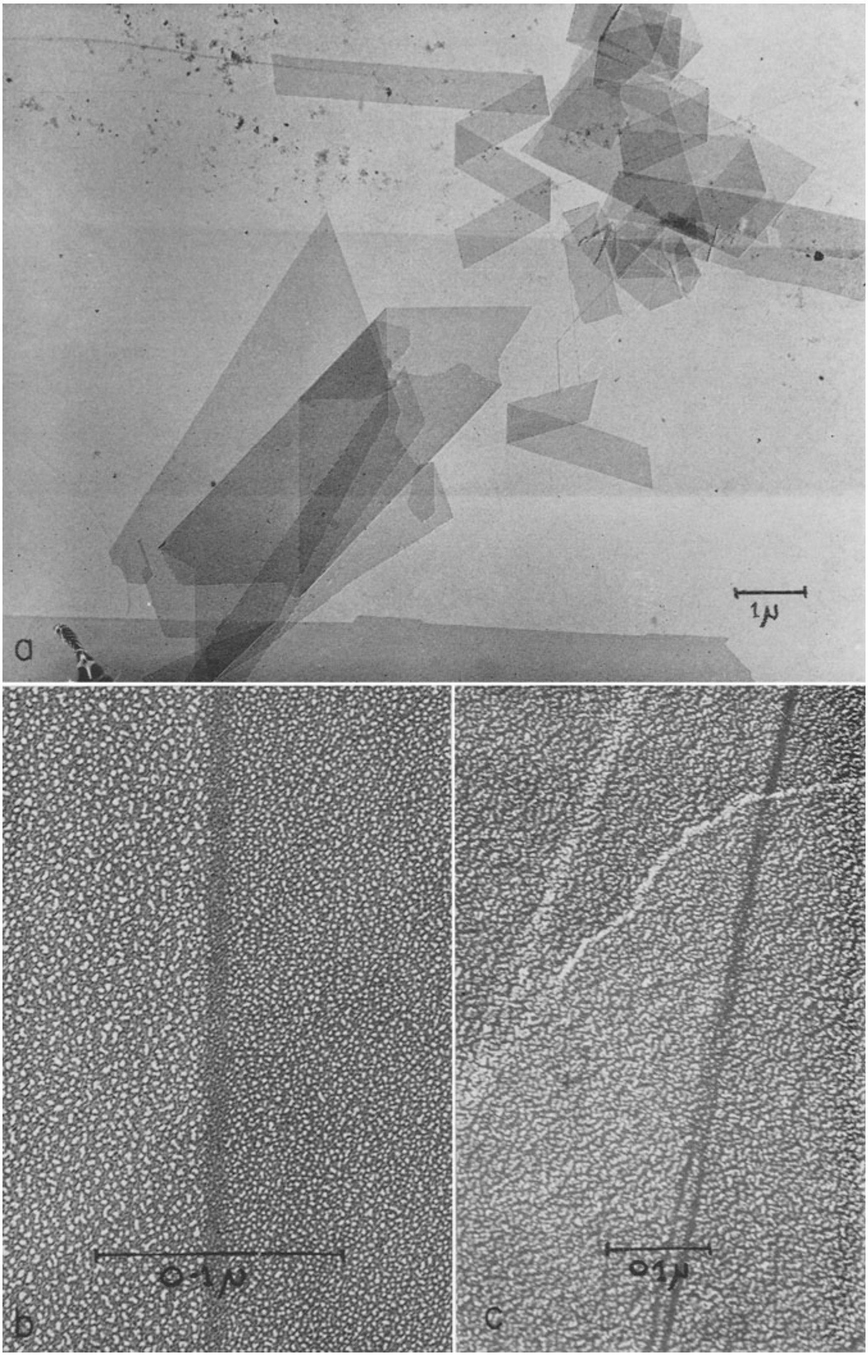

PLATE 2.—(a) Electron micrograph of D-allevardite, mounted as described in the text. 9200 ×; other data as for Plate 1. (b) Part of a flake of D-allevardite, showing a shadow suitable for measurement. The allevardite is on the left, mica substrate on the right. Platinum–iridium shadowing, cast at an angle of 11°. Magnification 320,000 ×, negative print. (c) Part of a flake of A-allevardite, showing an 18 Å edge dividing into two 9 Å edges as a result of cleavage and movement between two adjacent 2:1 sheets. Shadowed with platinum cast at an angle of 11°. Magnification 140,000 ×, negative print.

After evaporation of the metal film, the preparations were coated with a layer of carbon 50–100 Å thick, evaporated by the method of Bradley (1954) from a source approximately normal to the shadowed mica flakes. The composite metal–carbon film, with the clay flakes, was then stripped onto a water surface, recovered on seven-hole platinum electron microscope mounts, air dried, and examined at a magnification of 80,000 diameters in a Siemens electron microscope. Suitably oriented grains were photographed at this magnification and the width of the shadows estimated on prints at 300,000 ×, using a scale with 0.5 mm graduations and a 5 × hand magnifier.

TABLE 1.—MEASUREMENTS IN ÅNGSTRÖMS OF THE FLAKE THICKNESS OF A-ALLEVARDITE

	Observer 1	Observer 2	Mean Value
Large Step	18	18	18
Small Step	9	10.5	10
Increased Shadowing Metal	27	25	26

The flake thickness could then be estimated directly from the magnification and the known shadowing geometry. The precision of measurement was increased by keeping the thickness and grain size of the evaporated metal film to a minimum. To achieve this the preparations were pumped for at least two hours at a pressure of 10^{-4} mm Hg before attempting evaporation, and only just enough metal was used to give an easily measurable shadow. The importance of keeping the metal film thin is obvious from Table 1, which shows how deliberately increasing the amounts of shadowing metal greatly increased shadow length. Without special apparatus it is difficult to estimate the thickness of evaporated metal films of this kind, and no attempt was made to do so, as it was found sufficient to judge the thickness by eye from the optical density of the film in transmitted light. The best thickness gave a barely perceptible gray tint to the slide bearing the mica flakes; in the electron microscope the groups of metal atoms in such preparations were seen to be more widely spaced on the allevardite flakes than on the mica substrate (Plate 2, b).

The electron microscope was operated with double condenser illumination set to provide an illuminated area on the specimen approximately 20 μ in diameter. This provided a good compromise between the rapid contamination and consequent loss of contrast that takes place with the smallest illuminating spot, which is some 2 μ in diameter, and the equally rapid increase in granularity that could be observed when specimens were illuminated with the normal single condenser system at the high intensity needed for work at 80,000 ×.

When shadow lengths were measured directly from the original plates with a low-power microscope, errors inherent in making a photographic enlargement were avoided; however, the loss in contrast in the optical system of the microscope was so great that it was easier to measure from prints at 300,000 × with a 5 × hand lens than from plates at 80,000 × with a 20 × microscope. Shadow lengths were also successfully estimated by cutting out and weighing the shadows from the 300,000 × prints and calculating the shadow length from the weight, width and density of the cut-outs.

EXPERIMENTAL RESULTS AND DISCUSSION

Table 2 shows that the mean values of flake thickness for the three allevardite specimens agree well with estimates of the basal repeat distance of the unexpanded lattice obtained by X-ray diffraction. Thus there is little doubt that dispersion of the three minerals produces in suspension flakes equal in thickness to the basic structural unit of two 2:1 layers. This result is strikingly confirmed by the presence of a double step on the flake edge illustrated in Plate 2 (c); corresponding measurements are recorded under the heading of small and large steps in Table 1. Edges that were undivided and therefore suitable for measurement were sometimes difficult to find. The measurements in Tables 1 and 2 were therefore sufficiently precise to distinguish between flakes corresponding to single and double 2:1 layers. This is of considerable mineralogical interest, both for allevardites and for the thinner flakes of montmorillonite. Measurements made on selected montmorillonite samples confirmed that dispersion of the sodium form results in the separation of some flakes consisting of single 2:1 layers.

TABLE 2.—MEASUREMENTS IN ÅNGSTRÖMS OF FLAKES OF THREE ALLEVARDITE SPECIMENS

Sample	Flake Thickness from Shadow Lengths (I)	(II)	(III)	(IV)	(V)	Mean Value	X-ray Diffraction Data: $d001$: collapsed lattice[1]
A-allevardite	19	19	24	18	17	19.5	19.3
B-allevardite	26	25	22	19	24	23	19.3
D-allevardite	22	20	18	19	19	19.5	19.3

[1] Specimens were heated to 600 °C prior to X-ray examination.

When the experimental conditions described in this paper are used, the precision of measurement is limited to about ± 4 Å. For more precise estimates of flake thickness, errors arising from lack of sharpness of the shadow edges and from the presence of very small material in contact with the flakes will have to be still further reduced. There is little information on the effect of different vacuum conditions on the quality of evaporated metal deposits, but Bachmann *et al.* (1960) showed that much more sharply defined shadows may be obtained by using pressures as low as 10^{-8} mm Hg, although their thin platinum films prepared at this low pressure had a much larger grain size than those made at 10^{-5} mm Hg. The presence of very small material in the suspension, the second source of error mentioned above, has been observed with all preparations of allevardites and montmorillonites (Bates, 1958). This small material appears to be produced by the breakdown of the flakes during suspension in water. D-allevardite contained the least very small material of the three allevardites and all the montmorillonites so far examined contained more than any of the allevardites. Plate 1 (b) and Table 2 show how a coating of this very small material increased the apparent thickness of the B-allevardite flakes.

In conclusion, although an improvement in technique may produce more clearly defined shadows, and thus improve the precision of measurement on certain allevardites, it seems unlikely that montmorillonite suspensions can ever be freed sufficiently from very small materials to permit really precise measurements of flake thickness.

ACKNOWLEDGMENTS

We wish to thank Mlle. Caillère, Muséum d'Histoire Naturelle, Paris, Dr. Claringbull, British Museum (Natural History), London, and Mr. Kotelnikov, Institute of Geology, Moscow, for gifts of the minerals used in this study.

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