

The morphology of the Unter-Rupsroth montmorillonite.

(With Plates XIV and XV.)

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Summary. Electron micrographs of Na-saturated Unter-Rupsroth montmorillonite show that many of the individual flakes, which are probably 10 Å. thick, have straight edges meeting in 120° angles. This is evidence in support of the pseudo-hexagonal structure of montmorillonite. Similar pictures were obtained with Li-saturated clay and with 'Calgon'-dispersed material. The usefulness of electron microscopy for the study of clay mineral morphology depends upon the efficiency of dispersion and the details of the mounting techniques rather than the nature of the exchange cation or the particular dispersing agent employed.

THE mineral is a montmorillonite from Unter-Rupsroth in the Rhöngebirge, Germany.¹ It is a product of late hydrothermal alteration, and occurs as a pink material in veins in columnar phonolite, and also as a cavity mineral with calcite, chabazite, natrolite, and analcime in a different variety of the phonolite.

Chemical analysis shows a low iron content (Fe_2O_3 0.43, FeO 0.00, MgO 2.13 %), so that the mineral is an intermediate in the montmorillonite-beidellite series. The X-ray powder patterns are those of a typical well-crystallized montmorillonite,² and show (*hk*) bands, a 9.5 Å. basal spacing when heated to 500° C., and up to fourteen orders of the basal 17.7 Å. spacing with a glycerol-treated oriented aggregate. In its natural state the exchange cation is predominantly calcium, and the exchange capacity³ is 113 milliequivalents per 100 g.

Experimental methods. The natural clay was dispersed by adding one drop of a 5 % solution of sodium hexametaphosphate ('Calgon') to 20 mg. of clay in water. After shaking to complete dispersion the suspension was centrifuged at 10,000 *g* for 10 minutes, the supernatant liquid rejected, and the pellet dispersed in distilled water. If this was not done the micrograph was spoiled by the excess 'Calgon'. Sodium- and

¹ F. Heide, *Chemie der Erde*, 1927, vol. 3, p. 91. G. Nagelschmidt, *Min. Mag.*, 1938, vol. 25, p. 140.

² D. M. C. MacEwan, in *X-ray Identification and Structure of Clay Minerals*. London, Min. Soc., 1951 (p. 101).

³ R. Greene-Kelly, *Min. Mag.*, 1955, vol. 30, p. 604.

lithium-saturated clays were prepared by repeated washings with normal chloride solutions followed by alcohol and water mixtures until chloride-free. The clay was finally washed in absolute alcohol, dried, and then dispersed in distilled water.

A glass slide was coated with a suitable spreader, such as 'Teepol R' (Shell Chemicals Ltd.), polished with a soft cloth, and a drop of clay suspension was spread over its surface with a glass rod and allowed to dry as a thin film. The slide was then shadowed with either platinum or palladium and coated with a carbon film.¹ Immediately after removal from the vacuum the composite metal-carbon film bearing the clay particles was floated off on to a water surface, whence it was recovered on electron-microscope specimen grids in the usual way.

Results and discussion. The micrographs are shown as negative prints, in which shadows appear dark and heavy deposits of metal white. The direction of shadowing shown by the arrow in pl. XIV was obtained from the pointed edge of the fold shadows, and the shadowing angle to the clay surface is 7° ($= \tan^{-1} 1/8$). Measurement of the maximum shadow length on the thinnest clay layers gives a layer thickness of $15 \pm 5 \text{ \AA}$., but if the shadows of the thinnest layers from pls. XIV and XV are compared it will be seen that they differ, even though the angles of shadowing and the magnifications are similar. This is not interpreted as meaning that there are different numbers of layers in different pictures, but rather that a precise calculation of layer thickness is not possible where the thickness of the shadowing metal is as great as or greater than that of the layer itself. It seems fairly certain from this and other work that the thinnest layer seen is 10 \AA ., or one mica-layer thick.

In pl. XIV most of the cleavage flake edges are ragged and show no relation to crystal symmetry, but there are at least 17 angles or re-entrant angles of $120 \pm 5^\circ$ bounded by straight edges. These are considered to reflect the pseudo-hexagonal symmetry of the mica layers, and to be analogous to the hexagonal mica cleavage flakes seen in hand specimens and thin sections. The existence of these angles and edges is direct evidence in support of the widely accepted structure for montmorillonite,² which places it with the mica group of minerals containing sheets of silicon-oxygen tetrahedra with hexagonal symmetry. Similar angles of 120° were first reported by Mathieu-Sicaud *et al.*³ in electron

¹ D. E. Bradley, *Nature*, 1953, vol. 171, p. 1076.

² D.M.C. MacEwan, *loc. cit.*, p. 87.

³ A. Mathieu-Sicaud, J. Mering, and I. Perrin-Bonnet, 1951, *Bull. Soc. franç. Min. Crist.*, vol. 74, p. 439.

micrographs from dilute Na-montmorillonite suspensions, but they cannot be seen clearly in the published pictures. In pl. I, facing p. 456 of their paper, they showed a continuous film of material, in which individual flakes, although poorly defined, appear to be similar to montmorillonites from Redhill, Surrey, and from Wyoming. In our experience straight edges and angles of the kind described here are rarely found in these clays.

Other features of interest include the size of the flakes and their folding. The larger flake in pl. XIV is about $3\mu \times 4\mu$, and this is not exceptional for the material. It is appreciably larger than Wyoming bentonite, hitherto regarded as a montmorillonite of large particle size. The height of the folds, obtained from their shadows, varies between about 100 and 200 Å., and is probably the maximum curvature the silicate sheets can maintain. This folding, which is quite common in montmorillonites, must arise from the thinness of the sheets; the ratio of length or breadth to thickness for the large sheets in pl. XIV is 3 or 4μ to 10 Å., a ratio of about 3000:1. The analogy with a sheet of paper folded back is enhanced by the tears in the silicate sheet where the fold does not quite reach to the edge of the flake. In the centre of the field two sets of sub-parallel folds give a 'basket' effect, and an overlying flake follows the contours of the folds closely, leaving little or no interstitial space. It is also noticeable that whereas folds with their maximum curvature facing the source of platinum show a bright line caused by an accumulation of metal, those facing the other way show a double shadow effect suggesting a concave surface on the side of lower curvature, towards the centre of the flake.

The second plate is included to illustrate the effect (or rather, lack of effect) of different exchangeable cations on the morphology of the mineral. We have shown that complete dispersion results in flakes one mica-layer thick, and to describe montmorillonites we have reserved the term morphology for descriptions of the shape of these single layers. T. F. Bates¹ mentioned that the shape of particles of montmorillonite depends upon the nature of the dispersing agent, the exchange cation, and the grinding procedure. The inference that Na-saturated montmorillonites have poor particle outlines has not been confirmed in recent work at Rothamsted. On the contrary, micrographs showing the straight edges and well-defined angles illustrated here have also been obtained with the Black Jack mine beidellite and occasionally with Wyoming

¹ Clays and Clay Technology, Calif. Div. Mines, San Francisco, 1955, Bull. 169, p. 130.

bentonite. This is in agreement with a recent note by R. Roy and L. B. Sand,¹ which includes a micrograph of a synthetic Na-beidellite that has clearly outlined lath-shaped particles with straight edges.

To test whether exchanging the cation affects morphology, the micrographs reproduced in pl. XV were taken. No difference can be seen between Li-montmorillonite dispersed in water and the Na material of pl. XIV, or between these and the 'Calgon'-dispersed natural Ca-clay, although it is probable that dispersion with 'Calgon' entailed exchanging Na for Ca. This possibility of exchange also exists with other commonly used dispersing agents, which in addition are much less effective than 'Calgon'. An attempt to disperse the Ca-clay in water using super-sonic shaking at 25 kc. failed, and the resulting micrographs showed large aggregates. Similar pictures were obtained with the Li-clay when it was insufficiently dispersed in water, although complete dispersion gave the micrographs shown in pl. XV.

The evidence presented here suggests that the state of dispersion of the material and the technique used for making the electron-microscope mounts of montmorillonite have a major effect on the usefulness of the resulting pictures for studies of particle morphology. In our experience these factors are more important than the nature of the exchangeable cation or the particular dispersing agent employed.

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EXPLANATION OF PLATE XIV.

Electron micrograph of Unter-Rupsroth montmorillonite, negative print. Specimen Na-saturated, water dispersed. Shadowing: platinum at 7° to the clay surface. The arrow indicates the direction of shadowing.

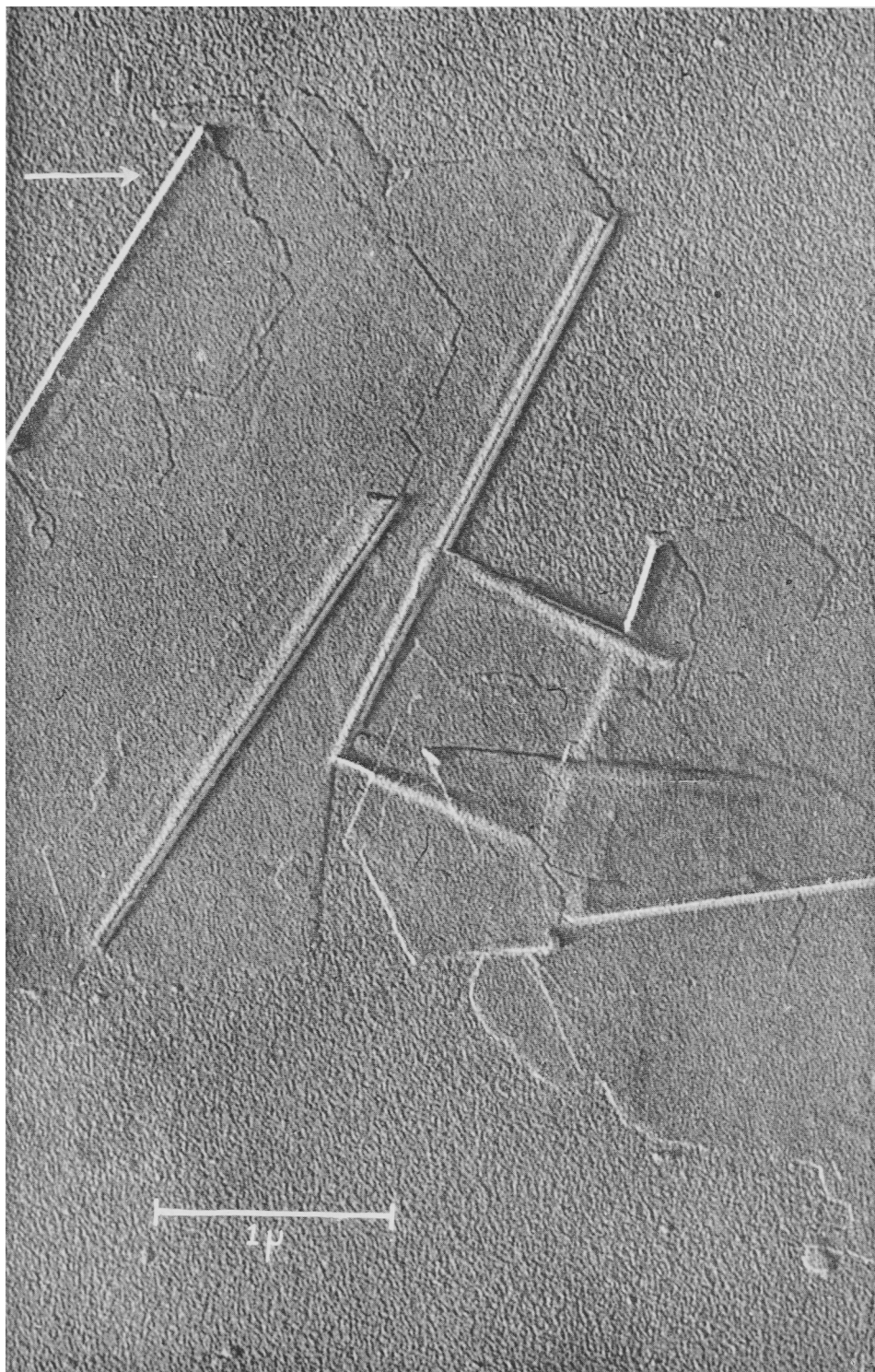
EXPLANATION OF PLATE XV.

Electron micrographs of Unter-Rupsroth montmorillonite, negative print.

A, B. Specimen Li-saturated, water dispersed. Shadowing: platinum at 7° to the clay surface.

C. Specimen natural clay, mainly Ca, Calgon dispersed. Shadowing: palladium at 7° to the clay surface.

¹ Amer. Min., 1956, vol. 41, p. 505



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