Clays and Clay Minerals, 1972, Vol. 20, pp. 83–88. Pergamon Press. Printed in Great Britain

ELECTRON OPTICAL OBSERVATIONS ON MARBLEHEAD ILLITE

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(*Received* 8 *September* 1971)

Abstract—Electron optical observations on Marblehead illite showed the presence of twinned aggregates of lath-shaped crystallites. The selected area diffraction patterns of these aggregates indicate a strict orientational relationship between them.

Original twinned mica flakes display all possible stages of the transformation of these micas into lath-shaped illites, where the *a* and *b* dimensions of layers do not show any noticeable changes, but *c*-dimension becomes shortened in the illites. The transformation seems to involve parting along (110) of the micas, subsequent H_2O and OH inclusion in the structure and other possible chemical changes resulting from the hydration. The morphology and the size of lath-shaped crystallites displaying (001) and (110) forms seem to be responsible for the excess of water and K-deficiency in the Marblehead illite compared to the micas.

Individual illite laths commonly have a length 0·1–4 μ, a width of 0·01–0·1 μ and a thickness varying between 10 and 50 Å.

INTRODUCTION

ILLITES are characterized with an excess of water and deficiency in K_2O compared to the micas. The position of this excess water (H_2O^+) in the illite structure has been subject to many speculations: For example, (H_3O^+) has been proposed to proxy for the interlayer cation (Brown and Norrish, 1952). It was also suggested that the excess water is trapped as neutral H_2O in interlayer cation positions which are not occupied by K^+ (Hower and Mowatt, 1966).

Pure well-crystallized illites are very rare. However such an illite was reported by Gaudette (1965) and Gaudette *et al.* (1966). Chemical composition, optical properties, X-ray diffraction and other analytical data together with the description of the geological occurrence were given by these investigators. According to them this illite occurs as large pockets of laminated clay in Silurian dolomite. It has a $2M_1$ stacking sequence and contains 5% or less expandable layers as mixed layering. Well crystallized flakes (original micas) of the sample were found optically to be biaxial negative with a $2V$ of approximately 5°. Its refractive indices were $\beta = 1{\cdot}537(2)$ and $\gamma = 1{\cdot}575(2)$. The chemical formula has been calculated to be:

$$(K_{0{\cdot}68}Na_{0{\cdot}03}Ca_{0{\cdot}05})(Si_{3{\cdot}54}Al_{0{\cdot}46}) \times (Al_{1{\cdot}50}Fe^{3+}_{0{\cdot}04}Fe^{2+}_{0{\cdot}07}Mg_{0{\cdot}36}Ti_{0{\cdot}05})O_{10}(OH)_2.$$

The above analytical data justify the Marblehead illite as a standard mineral for the illite group. Therefore it seemed worthwhile to investigate this sample further with electron optical methods and with a precise analysis of X-ray diffraction data.

ELECTRON OPTICAL OBSERVATIONS

A JEM 7 electron microscope equipped with a field limiting aperture permitted selected area diffraction (SAD) patterns from areas of the clay particles as small as one micron square. Furthermore at optimum optical conditions it was possible to observe morphology of clay particles with a resolution of 10–20 Å in bright field transmission images. Since the results of electron optical observations on clay particles are often affected by the pretreatment, a mixture water and tertiary butylamine in the ratio 700:1 was used. This mixture proved to be an excellent peptisator (Serwatzky, 1962) because the suspension spreads over the formvar film and after evaporation of the liquid the clay particles are better spread over the support film. Under vacuum some of the grids were coated with carbon and others with gold to an estimated thickness of about 50–60 Å. The following observations were made on the samples with an electron beam accelerated at 80 kV.

Figure 1 displays typical twinned aggregates of Marblehead illite where twin individuals form a trigonal arrangement. Each twin individual consists of a bundle of parallel lath-shaped crystallites. Twin individuals do not have however equal volumes. The crystallites are characterized by their extreme-

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ly small dimensions: The lengths vary from 0·1 to 4 μ, the widths between 20 and 100 Å. The thickness varies from 10 to 50 Å as they are measured from the shadows cast by gold coating at 2:1 angle. Thus individual lath-shaped crystallites have only a few 10 Å layers in their thickness and several unit cells in their widths. The superimposed SAD pattern of the sample, which was taken on the same plate, gives a diffraction pattern similar to that of a single crystal. This indicates that the lath-shaped crystallites have strict orientational relationships to each other within each twin individual. It is now very easy to determine the crystallographic orientation of single crystallites directly from the image and superimposed diffraction pattern where the *b*-axis can be chosen as any one of the three hexagonal directions. However it is important to allow for rotation of the diffraction pattern with respect to the image. This is caused by the change in strength of the intermediate lens. A test crystal of molybdenum trioxide was used for this purpose and the rotation was found to be 28° counterclockwise. Since the laths were deviating from the reciprocal lattice directions indicated in Fig. 1 by about 2°, the correction for the diffraction brought them almost to perfect alignment with the reciprocal lattice directions. Figure 2a has been obtained after applying this correction (28°) and after transforming reciprocal lattice directions into the real lattice directions. This figure shows that the lath-shaped illite crystallites are oriented parallel to the [$\bar{1}$10], [110] and [100] directions in reference to the $2M_1$ unit cell.

A larger and twinned mica flake is shown in Fig. 3. Under the electron microscope one can see various stages of transformation from the original twinned micas into lath-shaped crystallites. The twinning of the illite aggregates seems therefore to be inherited from the original micas. However not all the crystallites display a strict regularity in their orientation; partial and completely disordered arrangements of lath-shaped crystallites are also observed where the superimposed SAD pattern gradually changes from spot to ring pattern.

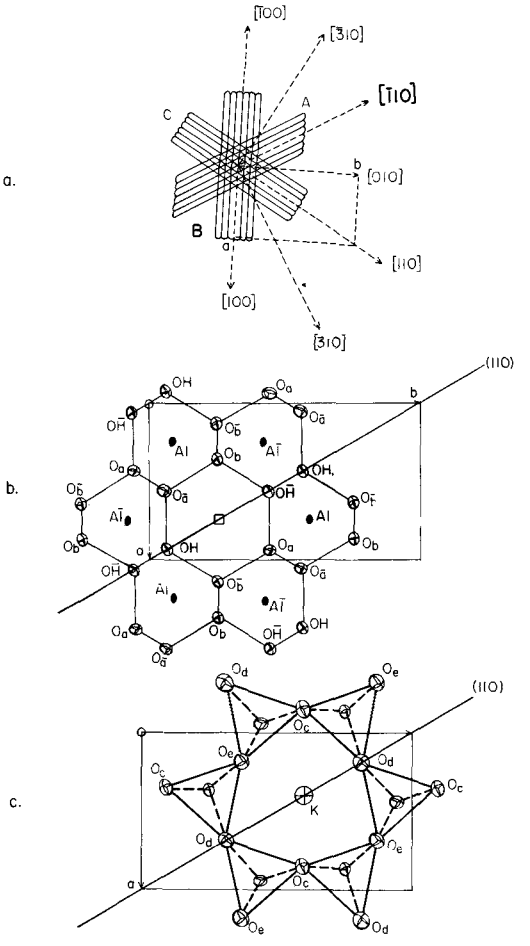


Fig. 2. (a) Orientation of illite aggregates consisting of lath-shaped cyrstallites with respect to the lattice directions of the $2M_1$ unit cell. (b) The trace of the (110) plane, which is parallel to one set of lath-shaped crystallites in Fig. 2a, in the octahedral sheets of $2M_1$ muscovite. This pseudo mirror plane passes through OHs and vacancies in octahedral sheets. (c) The trace of the (110) plane in the tetrahedral sheets passing through K and O_D oxygens which are known to be tilted in $2M_1$ dioctahedral micas.

LEAST-SQUARES ANALYSIS OF X-RAY POWDER DIFFRACTION DATA

In order to obtain precise X-ray diffraction data a Philips powder diffractometer was carefully aligned and a scintillation counter was used as a detector with a pulse-height-analyzer narrowed to a 3·3 V window. Scanning speed was 1° per min; receiving and antiscatter slits were 0·006″ and 1·0° respectively. Oriented slides of Marblehead illite were prepared on porous ceramic plates in order to obtain well resolved 001 reflections. In order to obtain *hkl* reflections, randomly (!) oriented powdered samples from the fraction smaller than 2 μ were prepared in standard aluminum holders. X-ray diagrams of powdered samples display several overlapping reflections which prevent unambiguous indexing and location of exact peak positions. Therefore relative intensities of all possible reflections within sphere of $2\theta = 77°$ are calculated and compared with the observed X-ray diffraction diagrams. Within $2\theta = 77°$ there are 258 allowed reflections for the CuK_α-radiation in the space group $C2/c$, which is the accepted space group for $2M_1$ illite. From these 258 reflections only strong

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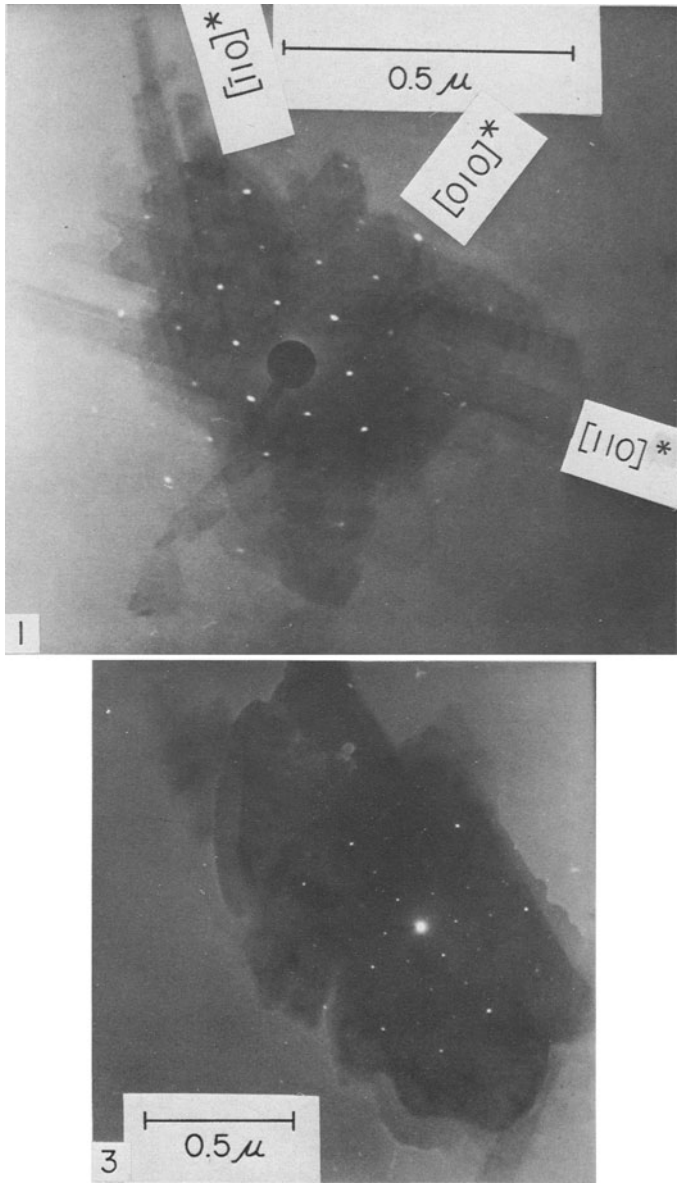


Fig. 1. Transmission electron bright field image of an illite aggregate from Marblehead. The SAD of the same aggregate is superimposed showing the strict orientational relationships of lath-shaped illite crystallites with respect to each other.

Fig. 3. Original twinned mica flake in Marblehead illite sample.

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reflections are observed on the powder patterns. Table 1 lists 68 expected reflections of strong intensities together with the observed ones. The structure factors (F_c) were calculated with the RFINE computer program (Finger, unpublished) using the $2M_1$ phengite atomic parameters (Güven, 1967). The precise cell parameters were then computed by a least squares refinement program (Appleman *et al.*, unpublished) which can also index certain unindexed reflections. The cell parameters of Marblehead illite obtained in this way are given in Table 2. This table also contains the cell parameters of $2M_1$ phengite and $2M_1$ muscovite (Güven, 1967).

As mentioned above there are uncertainties in the location of peak positions and in the indexing of clay mineral reflections obtained by X-rays. Selected area diffraction with electrons as discussed in the following section may be very helpful in removing these uncertainties.

Precise cell parameters indicate that a and b dimensions of Marblehead illite are close to those of phengite. The c dimension of illite is significantly shorter than that of phengite. The shortening of the c-axis in phengite in comparison to that of muscovite is attributed to the decreased tetrahedral tilt in phengite (Güven, 1967). This may also contribute partly to the shortening of c-axis in Marblehead illite. Another factor which may contribute to that is the K-deficiency in illites.

SELECTED AREA DIFFRACTION ON MARBLEHEAD ILLITE

Electron diffraction on selected areas of about 1 μ square of the clay flakes can give significant diffraction data with much better resolution than X-ray powder diffraction for the (hk) reflections. From the electron diffraction diagrams the tan 2θ of the diffraction angle is directly measured as $D/2L$ where D is the ring diameter and L is the effective camera length.

The interplanar spacing is then exactly given by the following relationship (Andrews *et al.*, 1967)

$$d = \frac{2\lambda L}{D}\left[1+\frac{3D^2}{32L^2}\right] \qquad (1)$$

Table 1. Calculated and observed X-ray reflections with strong intensities which may occur on X-ray diffraction powder patterns of illites (Diffraction angles below $2\theta = 77°$ are given for CuK_α = 1·54178 Å)

h	k	l	F_c	$2\theta_c$	$2\theta_{obs.}$	h	k	l	F_c	$2\theta_c$	$2\theta_{obs.}$
0	0	2	61	8·95	8·86	$\bar{2}$	0	6	125	42·18	42·20
0	0	4	103	17·95	17·84	1	3	5	130	42·58	42·56
1	1	0	80	19·80	19·80	0	0	10	221	45·92	45·86
$\bar{1}$	1	1	99	19·91		$\bar{1}$	3	7	96	46·22	
0	2	1	55	20·17		2	0	6	102	46·86	
0	2	2	48	21·64		$\bar{2}$	2	8	66	52·62	
$\bar{1}$	1	3	74	22·97		$\bar{1}$	3	9	105	53·18	
0	2	3	80	23·89		2	0	8	96	53·91	53·96
$\bar{1}$	1	4	111	25·61	25·44	2	4	0	70	53·92	
0	2	4	91	26·75		2	2	7	63	54·47	
0	0	6	166	27·07	27·06	$\bar{3}$	1	3	61	54·63	
1	1	4	124	28·03		$\bar{2}$	0	10	197	55·57	55·60
0	2	5	138	30·05	29·90	1	3	9	198	56·20	
1	1	5	108	31·47	31·48	$\bar{1}$	5	4	97	56·50	
$\bar{1}$	1	6	110	32·26	32·28	0	6	0	221	61·62	61·64
$\bar{1}$	3	1	139	34·55		$\bar{3}$	3	1	227	61·82	61·80
2	0	0	137	34·72	34·74	2	0	10	128	61·97	
$\bar{2}$	0	2	156	34·98		3	3	1	73	62·74	
1	3	1	146	35·03	35·00	2	2	10	77	65·70	
1	1	6	65	35·22		0	0	14	87	66·20	
$\bar{1}$	3	3	118	36·48		0	4	12	118	70·81	
2	0	2	118	36·85		2	0	12	207	70·94	
$\bar{2}$	0	4	145	37·60	37·54	$\bar{2}$	2	13	105	71·85	
1	3	3	154	37·84		2	6	0	138	72·71	
$\bar{2}$	2	1	75	40·06		$\bar{4}$	0	2	158	72·86	72·84
0	4	1	51	40·20		$\bar{2}$	6	2	155	72·87	
2	2	0	48	40·21	40·26	4	0	0	150	73·28	
$\bar{1}$	3	5	49	40·52		$\bar{3}$	3	9	108	73·37	
2	2	1	72	40·90		$\bar{4}$	0	6	122	76·38	76·40
0	4	2	60	41·01		2	6	4	113	76·73	
$\bar{2}$	2	3	72	41·36							

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Table 2. Unit-cell parameters and chemical formula of the two dioctahedral micas and illites on the basis of $O_{10}(OH)_2$ (Standard errors are given in parenthesis)

	Georgia muscovite	Tiburon phengite	Marblehead illite	
Interlayer	$K_{0.86}Na_{0.10}(H_3{}^+O)_{0.01}$	$K_{0.87}Na_{0.07}Ba_{0.01}Ca_{0.02}$	$K_{0.68}Na_{0.03}Ca_{0.05}$	
Tetr. layer	$Si_{3.02}Al_{0.98}$	$Si_{3.39}Al_{0.61}$	$Si_{3.54}Al_{0.46}$	
Oct. layer	$Al_{1.9}Mg_{0.06}Fe^{2+}_{0.05}Fe^{3+}_{0.02}Ti_{0.01}$	$Al_{1.43}Mg_{0.50}Fe^{2+}_{0.09}Fe^{3+}_{0.05}Ti_{0.01}$	$Al_{1.5}Mg_{0.36}Fe^{2+}_{0.07}Fe^{3+}_{0.04}Ti_{0.05}$	
			X-ray diff.	electron diff.
a, Å	5·1906(2)	5·2112(3)	5·195(1)	5·20(1)
b, Å	9·0080(3)	9·0383(4)	9·030(4)	9·06(2)
c, Å	20·0470(6)	19·9473(6)	19·868(8)	
β, in degrees	95·757(2)	95·769(5)	95·89(2)	
unit-cell volume, (Å^3)	932·61(8)	934·81(1)	927·1(5)	

For very thin clay flakes the reciprocal lattice points are elongated along the direction normal to the flakes resulting in reciprocal lattice spikes. The length of the spikes observable intensity is approximately given by $2/N.d_{hkl}$, where N is the number of (hkl) planes contributing to the reflection. For a flake of 50 Å thickness the spikes will have a length of 0·04 A^{-1} and c^* reciprocal lattice parameter for a two layered mica will be about 0·05 A^{-1}. Hence reciprocal lattice rows parallel to c^* form rods and the diffraction pattern approaches that of a two-dimensional lattice. The a and b unit cell parameters are then directly given on the micrographs by the relationship:

$$1/d^2_{hk} = h^2/a^2 + k^2/b^2. \qquad (2)$$

In order to obtain satisfactory results in the electron diffraction patterns it is essential to know the camera constant $(2\lambda L)$ in the equation (1) accurately. Variations in the camera constant are usually caused by fluctuations in the voltage supply and characteristics of the instrument. To improve the situation a metal has been used as internal standard. Gold has been preferred over Al and other metals which form oxides in air or may incorporate tungsten into their structures or become impure during the evaporation. By measuring superimposed diffraction patterns of the unknown and the standard, the interplanar spacing can be computed simply using the following approximation:

$$d_x \cong d_s \frac{D_s}{D_x}. \qquad (3)$$

Where D_s and D_x are ring diameters, that is the distances between reflections related by the center of symmetry in a single crystal pattern. The above mathematical approximation yields an error of 0·2% in the accuracy of the calculated d values.

For Marblehead illite a and b dimensions are calculated using relations 2 and 3 and gold reflection $d(111) = 2{\cdot}355$ Å was the internal standard line. Errors caused by lens aberrations and focusing conditions increase as the diffraction angle increases. In order to minimize these errors, only reflections with indices $h < |4|$ and $k < |6|$ were measured. Table 2 gives unit cell parameters obtained from the SAD along with those obtained by the X-rays.

DISCUSSION

Excess of structural water

The dimensions of the lath-shaped individual illite crystallites were described above. Because of these small dimensions the relationship between the morphology and internal atomic structure of illite crystallites becomes important. Referring to Fig. 2a and considering only the illite crystallites parallel to $[\bar{1}10]$ direction one can see that the laths are separated from each other along the (110) atomic plane, which passes through OHs and octahedral vacancies in dioctahedral micas (Fig. 2b). Thus the lath-shaped crystallites mostly expose (110) and (001) atomic planes, where OHs represent active sites to interact with cations as well as anions or water molecules through H-bonding. During the parting the OHs which are shared between two octahedral cations become detached from one of the octahedral cation. This probably involves further attachment of OHs or H_2Os to the octahedral cation which lost OH. Thus this may be one possible process which increases the OH content as well as active sites for exchange reactions.

The parting of a mica structure along (110) may cause the following changes on the plane of basal oxygens of dioctahedral micas: As seen on Fig. 2c this parting results in separation of the mica struc-

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ture along the K and O_D oxygen atoms. These O_D oxygens which were shared between two silica tetrahedra now leave one of the tetrahedra. This may cause attachment of OH or H_2O to the other silica tetrahedra in order to complete the coordination polyhedron. This process increase water content of the mica layer as well as the number of active O_D sites on the (001) plane.

Release of interlayer cation

It is well known that the interlayer cations are held by 12 oxygens from the top and bottom mica layers, of which 6 nearest oxygens form an octahedral coordination polyhedron. Since the illite crystallites have a thickness of only a few mica layers, those interlayer cations on the large surface areas of (001) atomic planes are somewhat less strongly bonded to the mica layers. The parting of atomic planes after (110) also break bonds between the interlayer cation and the surface oxygens, which further contributes to the release of interlayer cations.

Thus the morphology and the dimensions of illite individual crystallites which practically display only the (110) and (001) forms seem to contribute appreciably to the increase of structural water and exchange capacity as well as to the K-deficiency of this clay mineral in Marblehead illite.

Origin of lath-shaped Illites

Illites of similar morphology were previously reported by Weaver (1953), Rex (1966), and Jasmund *et al.* (1969) as authigenic formations in hydrothermally altered sandstones. The formations of these illites were attributed to alteration of K-feldspars by Weaver (1953) in Oswego graywacke and Rex (1966) in several sandstones. Jasmund *et al.* (1969) related the origin of lath-shaped illites to decomposition of muscovite by parting after (110) and subsequent chemical changes. In the above discussion it is also assumed that original mica is disintegrating by parting after (110) and this is followed by chemical and structural changes. The chemical composition of the Marblehead sample suggests a phengitic character of the original mica. Internal strains in dioctahedral mica structures may also contribute to the parting and hydroxylation mentioned above. Especially in dioctahedral micas of phengitic composition there are larger polyhedral strains in octahedral layers because of substitutions of Al by larger cations like Mg and Fe^{2+}. Compositional and structural relationships between illites and phengites were previously discussed (Güven, 1970). The alteration of this mica to illites can proceed in a much simpler manner, as in the case of Marblehead, than the alteration of muscovite to illites. Phengitic and sericitic fine grained micas seem to have been overlooked as potential source materials for illite formation.

Acknowledgment—This work was financially supported by a Summer Faculty Fellowship from the University of Illinois.

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Résumé—Des observations en optique électronique de l'illite de Marblehead indiquent la présence d'agrégats maclés de cristallites en forme de lattes. Les diagrammes de diffraction de zones sélectionnées de ces agrégats montrent une relation stricte entre leur orientation mutuelle.

Les lamelles maclées du mica originel offrent toutes les possibilités pour la transformation de ces micas en illites en forme de lattes, puisque les dimensions *a* et *b* des couches ne subissent pas de changement notable, alors que la dimension *c* est plus petite dans les illites. La transformation semble impliquer une séparation selon (110) des micas, puis l'inclusion de H_2O et d'OH dans la structure, et d'autres modifications chimiques possibles résultant de l'hydratation. La morphologie et la taille des cristallites en forme de lattes montrant des formes (001) et (110) semblent responsables de l'excès d'eau et de l'insuffisance en K dans l'illite de Marblehead comparée aux micas.

https://doi.org/10.1346/CCMN.1972.0200206 Published online by Cambridge University Press

Les lattes individuelles d'illite ont couramment une longueur de 0,1 à 4 μ, une largeur de 0,01 à 0,1 **m** et une épaisseur variant de 10 à 50 Å.

Kurzreferat – Elektronenoptische Beobachtungen an Marblehead Illit ergaben die Anwesenheit verzwillingter Aggregate von lattenförmigen Kristalliten. Die ausgewählten Flächen-Beugungsbilder dieser Aggregate deuten auf eine streng richtungsmässige Beziehung unter denselben hin.

Ursprünglich verzwillingte Glimmerschuppen zeigen alle die möglichen Umwandlungsstufen dieser Glimmer zu lattenförmigen Illiten, wobei die *a* und *b* Dimensionen der Schichten keine wesentlichen Änderungen aufweisen, während die *c*-Dimension in den Illiten verkürzt wird. Die Umwandlung scheint eine Trennung entlang (110) der Glimmer, nachfolgenden H_2O und OH Einschluss in das Gefüge sowie weitere mögliche chemische Veränderungen infolge der Hydration zu umfassen. Die Morphologie und die Grösse der lattenförmigen Kristallite, die (001) und (110) Formen aufweisen, scheint für den Wasserüberschuss und die K-Verarmung im Marblehead Illit im Vergleich mit den Glimmern verantwortlich zu sein.

Einzelne Illit-Latten haben meist eine Länge von 0,1 bis 4 μ und eine Dicke, die zwischen 10 und 50 Å variiert.

Резюме — Электронноптическое исследование иллита из Марблхеда обнаружило присутствие двойниковых агрегатов лентовидных кристаллитов. Микродифракционные картины, полученные от этих агрегатов, указывают на наличие между ними строгих ориентационных соотношений.

Исходные сдвойникованные чешуйки обнаруживают все возможные стадии привращения слюд в лентовидные иллиты; при этом параметры *a* и *b* слоев не претерпевают заметных изменений, в то время как параметр *c* при переходе к иллиту сокращается. Превращение в иллит очевидно включает расщепление слюд по плоскости (110), последовательное внедрение H_2O и OH в структуру и другие возможные химические изменения, являющиеся следствием гидратации. Морфология и размеры лентовидных кристаллитов, ограниченных простыми формами (001) и (110), по-видимому, ответственны за избыток воды и дефицит K в иллите из Марблхеда по сравнению со слюдами.

Отдельные ленты иллита обычно имеют длину от 0,1 до 4 мк, ширину от 0,01 до 0,1 мк и толщину, изменяющуюся в пределах от 10 до 50 Å.

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