

## KAOLINITE FROM A BROOKLYN SUB- WAY TUNNEL\*

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### INTRODUCTION

A white clay forming small patches in deeply weathered rock is occasionally encountered in excavations east of the Harlem River and East River in New York City. Specimens of this material were recently examined and the white clay mineral identified as kaolinite, as strictly defined. The white clay furnishes evidence of interest concerning the origin of the mineral kaolinite, and adds another locality to the rather meagre list of those in which kaolinite has been recognized by modern methods.

### ACKNOWLEDGMENTS

The writer wishes to express his appreciation of the efforts of Mr. E. A. Kilinski, consulting geologist for the subway excavation, who collected specimens of the white clay and associated rock as the work advanced. It was also through Mr. Kilinski's efforts that an opportunity was offered to visit the locality during the progress of the work. Professor R. J. Colony of Columbia University has shown special interest in the study of the specimens and has offered numerous observations of value. The present account is an outgrowth of work on clay minerals carried on for the last few years in cooperation with Dr. Clarence S. Ross of the United States Geological Survey to whom the writer is greatly indebted for his generous suggestions. The portions of this description dealing with nomenclature are summarized from a joint paper in which Dr. Ross is the senior author, to be published shortly by the United States Geological Survey.

### THE SIGNIFICANCE OF KAOLINITE

The word *kaolinite* as herein employed is intended to signify common kaolin of the type found throughout the southeastern part of the United States and in numerous other places. Kaolinite has been subject to two different interpretations in mineralogical literature. A brief explanation is justified, therefore, in order to clarify the meaning of the word as used in this paper. Two dif-

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ferent minerals have been rather consistently called kaolinite. These may be designated as: (1) A clay mineral from the Isle of Angelesey investigated by Dick;<sup>1</sup> (2), A clay mineral of the type studied by Johnson and Blake.<sup>2</sup> Recent work<sup>3</sup> has demonstrated that these are two independent clay minerals differing in crystallization, physical properties and temperature of dehydration but having the same chemical composition. It has been suggested that the clay mineral from Angelesey be called *dickite* in recognition of the optical work of Allan Dick<sup>4</sup> who so ably recorded the properties of the mineral in 1888. The name kaolinite, it has been considered, should be retained for common kaolin which represents the type studied by Johnson and Blake.

TABLE 1.  
KAOLIN MINERALS

NAME	CHEMICAL COMPOSITION	X-RAY DIFFRACTION PATTERN	OPTICAL PROPERTIES
NACRITE	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	Distinctive	Distinctive from other minerals but nearly the same for dickite and nacrite.
DICKITE	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	Distinctive	
KAOLINITE	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	Distinctive from other minerals but identical for kaolinite and anauxite.	Distinctive from other minerals but nearly the same for kaolinite and anauxite.
ANAUXITE	$\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$		

(After Ross and Kerr)

In addition to *kaolinite* and *dickite*, two other minerals occur in the kaolin group, which show certain physical or chemical properties indicating relationship to *kaolinite* and *dickite*. These should be kept in mind in any discussion dealing with the identification of kaolin. The other two minerals are *nacrite* and

<sup>1</sup> Tookey and Dick, *Percy's Metallurgy Fuel*, 1875, and *Min. Mag.*, 8, 15, 1888.

<sup>2</sup> Johnson, S. W., and Blake, J. M. On Kaolinite and pholerite: *Am. Jour. Sci.*, 2nd Ser., Vol. 43, pp. 351-361, 1867.

<sup>3</sup> Ross, Clarence S., and Kerr, Paul F. The Minerals of Kaolin, (in press).

<sup>4</sup> Ross, Clarence S., and Kerr, Paul F. Dickite a kaolin mineral: *Amer. Min.*, Vol. 15, No. 1, pp. 34-39, 1930.

*anauxite*. *Nacrite* agrees in chemical composition with *kaolinite* and *dickite* but differs in crystallization (as shown by *x*-ray diffraction patterns). In addition it has somewhat different optical properties. *Anauxite* is probably isomorphous with *kaolinite*. It has nearly the same optical properties, and gives the same *x*-ray diffraction pattern as *kaolinite*, but contains materially different amounts of alumina and silica in the chemical formula. The relationship between these four minerals is summarized in table 1.

It will be noted in examining table 1 that no one method of identification, such as chemical analysis, *x*-ray study, or optical

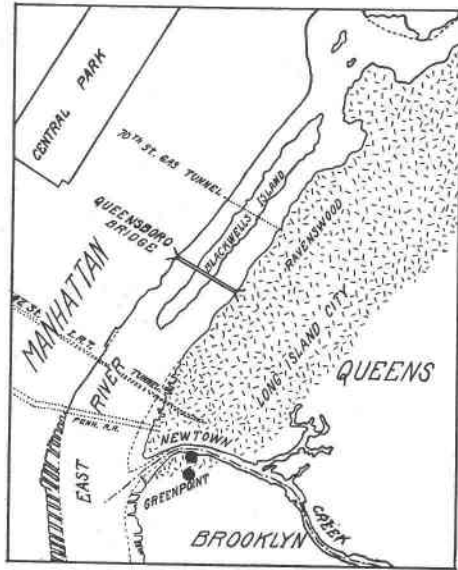


FIG. 1. Sketch map of Newtown Creek and vicinity showing the kaolinite localities and the approximate boundaries of the Ravenswood granodiorite.

examination is sufficient in all instances to distinguish these minerals from each other. On account of this situation, the identification of a kaolin should be approached with caution and should not be considered complete until at least two and preferably more methods of study have been exhausted.

#### LOCATION

The specimens examined were collected in the new city subway tunnel in the vicinity of Newtown Creek, along the boundary be-

tween the boroughs of Brooklyn and Queens (See Fig. 1). The new subway line consists at this point of two parallel tunnels extending north-south and excavated to a level below the bottom of Newtown Creek. The principal white clay localities occur in the west tunnel 50 and 550 feet, respectively, south of the U. S. Government bulkhead line of Newtown Creek. No exposures of rock are visible at the surface. The localities lie beneath buildings and alongside of the south approach to the vehicular bridge over the Creek at Vernon Avenue. All of the specimens examined were collected in the fall of 1928 and early in 1929. The tunnel has since been lined with concrete and new material is no longer available at this point.<sup>5</sup>

#### THE LOCAL GEOLOGY

Much has been written on the geology of Greater New York.<sup>6</sup> In these accounts both the surface geology and the areal distribution of the formations underlying the glacial drift have been mapped in considerable detail. The portion of Long Island in the vicinity of Newtown Creek is generally considered to be underlain by the Ravenswood granodiorite. The most recent and accurate records of the geology of this portion of the city are contained in discussions by Professor Berkey. In describing the formational units underlying the city, he states:

"Another is known to be of large areal extent in Long Island City and Brooklyn, extending beneath the East River into the Lower East Side of Manhattan. It is known to recent workers in the geology of New York City as the Ravenswood granodiorite. It is probably the most ancient igneous or strictly intrusive rock in New York City and is associated only with the Fordham Gneiss the oldest of all the formations in southeastern New York."<sup>7</sup>

<sup>5</sup> Since the above was written, Prof. W. M. Agar of Columbia University has observed another deposit of kaolinite about a mile south of Newtown Creek in a more recently excavated continuation of the same tunnel.

<sup>6</sup> See for instance: *Folio No. 83, U. S. Geological Survey*. Hobbs, W. H., *The Configuration of the Rock Floor of Greater New York: Bull. 270, U. S. Geological Survey*. Berkey, C. P., *Areal and structural geology of Southern Manhattan Island: (Part 2, pp. 247-282, Apr. 1910)*; *The Geology of New York City: Proc. Municipal Engineers of the city of New York, 1911*, pp. 5-39; *Geology of the New York City (Catskill) Aqueduct: New York State Museum Bull. 146, Feb. 1911*.

<sup>7</sup> Berkey, C. P., *The Geology of New York City, op. cit.*

The name Ravenswood granodiorite was first suggested by Professor Kemp,<sup>8</sup> who in writing a detailed description of a section across East River at Blackwells Island, along a gas company's tunnel stated:

"There is good reason to think the Ravenswood rock an intrusive hornblende-granite or granite-diorite, with which it agrees in mineralogical composition."

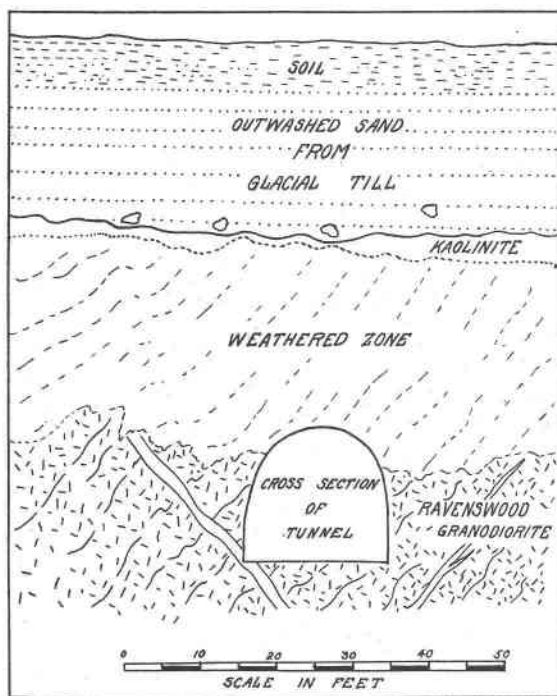


FIG. 2. Generalized section of the weathered and kaolinized Ravenswood granodiorite as it occurs beneath the glacial till.

Ziegler prepared a petrographic description of the Ravenswood granodiorite and mapped the areal extent of the intrusive under Professor Berkey's direction.<sup>9</sup> The distribution of the granodiorite shown in Figure 1 has been compiled from his report and from information furnished by Mr. E. A. Kilinski.

<sup>8</sup> Kemp, James F., The Geological Section of the East River at 70th St. New York: *Trans. N. Y. Acad. Sci.*, Vol. 14, p. 273.

<sup>9</sup> Ziegler, Victor, The Ravenswood granodiorite: *Ann. N. Y. Acad. Sci.*, Vol. XXI, pp. 1-10.

## OCCURRENCE OF WHITE CLAYS IN GREATER NEW YORK

It is only during tunneling or deep excavating operations that one is provided with an opportunity to examine the rock underlying the glacial drift in this area and to study types of alteration. The clay at Newtown Creek occurs in patches in a weathered zone below the contact between the underlying Ravenswood granodiorite, and overlying outwashed sand from glacial drift. The weathered zone varies from 15 to 35 feet in thickness where cut by the tunnel and is made up of the decayed granodiorite. The top of this zone is irregularly capped with a layer of white clay varying from a few inches to two feet in thickness. North of Newtown Creek in Long Island City other zones of decayed rock occur, but white clay was not encountered in cutting the tunnel.

White clays, probably of this type, have previously been reported by Humphreys and Julien<sup>10</sup> and also by Professor Kemp.<sup>11</sup> It appears from these previous descriptions and from field observations at this locality that the kaolinized areas are residual portions of a pre-glacial weathered surface not swept away by the glacier. Humphreys and Julien emphasized this pre-glacial age of the kaolinization. They reproduced a photograph of a nearly vertical kaolinized pegmatite dike, planed off by glaciation and overlain by glacial drift. An accompanying decay in the adjacent rock was reported, which from their description, corresponds to weathered zones along the subway tunnel.

The kaolin on Long Island is limited to the surface or near surface portions of the rock, and is not encountered in the deep tunneling operations beneath the city.<sup>12</sup> The alteration is apparently not restricted to one particular phase of the granodiorite, but extends laterally across both the granodiorite and the pegmatites by which it is cut. The distribution of the areas is erratic and seemingly without relation to the present topography. Portions of the underlying rock in which one would expect recent weathering action to be most active are often least altered.

Professor Kemp<sup>13</sup> encountered a number of kaolinized zones in the gas tunnel section beneath the East River at Blackwells Is-

<sup>10</sup> Humphreys, Edwin W., and Julien, Alexis A., Local decomposition of rock by the corrosive action of pre-glacial peat-bogs: *Jour. Geol.*, Vol. 19, No. 1, Jan.-Feb. 1911, pp. 47-56.

<sup>11</sup> Kemp, J. D., *op. cit.*

<sup>12</sup> Berkey, C. P., Statement in conversation.

<sup>13</sup> *Op. cit.*

land. A portion of his description at a point 430 feet from the west shaft along the waterfront at the foot of E. 70th Street reads as follows:

- “ 7 ft. white kaolinized pegmatite.
- 5 ft. soft black mud with lumps of lignite, with the next seven feet evidently filling a fissure.
- 2 ft. coarse river sand with abundant pyrites.
- 5 ft. sand and black mud with lignite and balls of pyrites.
- 22 ft. white kaolinized pegmatite with lumps of foetid quartz.
- 4 ft. same, streaked with chlorite.
- 11 ft. kaolinized pegmatite.
- 42 ft. soft green chlorite schist.”

Total 98 ft.

Samples of both white clay and the green chlorite (probably vermiculite) were examined by Professor Kemp who attributed the white clay to kaolinization of the pegmatite, and the green chlorite to decomposition of mica schist. Humphreys and Julien attribute the formation of the white clay and the deep local decay

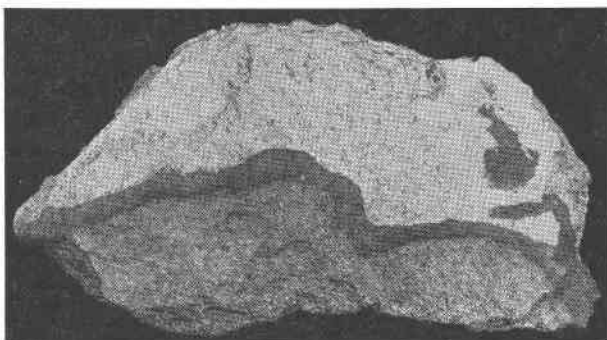


FIG. 3. (1/2 natural size.) Successive stages in the kaolinization of the granodiorite as exhibited in a hand specimen. The rock is evidently first decayed as shown in the lower half; then a limonitic band advances and the kaolinite and quartz shown in the upper half is the final product.

of the rock to the continuous corrosion of ancient pre-glacial peat-bogs. They mentioned the occurrence of remnants of such peat-bogs in a number of places throughout the area covered by Greater New York. The presence of bog-iron in some of these, they believe, indicates the early and long continued activity of organic acids in solution, removing, concentrating and depositing iron oxide from the surface of the rocks.

The occurrence of the kaolin in the decayed Ravenswood granodiorite is probably similar to that discussed by the authors mentioned above. It does not, however, appear to be limited to the alteration of pegmatites, as might be inferred from the East River occurrence, but corresponds more nearly to the occurrence at the intersection of Westchester Avenue and Southern Boulevard in the Bronx, described by Humphreys and Julien. Figure 2 illustrates the occurrence along the subway tunnel as interpreted from tunneling operations and drill holes.

The progress of the alteration can be observed in hand specimens as shown in Figure 3. A limonitic band separates the kaolinite from partially decayed granodiorite.



FIG. 4. Drawing of thin section  $\times 25$ . Hornblende (Ho), Orthoclase (Or), and Pyrite (Py) are the minerals present. A portion of the granodiorite containing a concentration of pyrite probably "magmatic" but later than the silicate minerals.

#### THE CHARACTER OF THE RAVENSWOOD GRANODIORITE

The texture of the rock is extremely varied, fine grained portions changing abruptly to coarsely crystallized patches having individual crystals an inch or more across. Irregular foliation and streaks of injected matter are prominent. The rock is traversed by numerous dikes which are unaltered below the zone of rock weathering.

Orthoclase, quartz, oligoclase, hornblende, and biotite are the most abundant minerals in the granodiorite. Microcline, apatite, zircon, garnet, titanite, and muscovite are scattered through the rock in minor amounts. Pyrite is frequently observed in more or less minor concentrated areas as a late magmatic product (Fig. 4). Some sericite may be seen in the pegmatitic phases or in areas



containing concentrations of feldspar. The minerals noted in the fresh and unaltered granodiorite are practically the same as those recorded by Ziegler.<sup>14</sup> Ziegler, however, evidently failed to encounter any considerable area of rock weathering or in any event

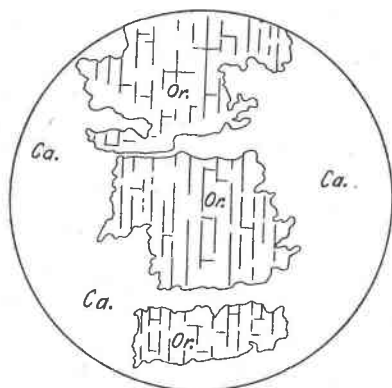


FIG. 5. Drawing of thin section  $\times 25$ . Orthoclase (Or) "etched out" and in part replaced. The filling in each instance consists of calcite (Ca). An alteration noted in both unkaolinized and partly kaolinized portions of the granodiorite.



FIG. 6. Drawing of thin section  $\times 25$ . Hornblende (Ho) subjected to attack and filling by calcite (Ca) and later removal of portions of the calcite with the formation of kaolinite.

did not discuss such a feature. He mentioned the introduction of carbonates, and included kaolin in his mineral list but did not go farther in his explanation.

<sup>14</sup> *Op. cit.*

Carbonate producing solutions evidently penetrated the rock at some time following its crystallization. Calcite filling "etched out" cavities in feldspar and hornblende is frequently observed in thin sections (Figs. 5 and 6). Crystals of calcite have also been found in openings in the rock along the walls of the tunnel. Possible sources of both calcium and magnesium carbonate may exist in adjacent unexposed areas of limestone. The complete history of the carbonate minerals is hidden. It does not appear, however, that these are a prerequisite to the later decay or weathering resulting in the formation of kaolinite.

#### KAOLINITE

The clay mineral is typical white kaolinite. It is soft, porous, adheres to the tongue, and goes to pieces when immersed in water.

It is for the most part finely crystalline, and a portion of a sample agitated in water and allowed to stand, will remain in suspension for several days. The largest amount of the clay, however, will settle in a few hours. All of the suspended particles settle rapidly, however, when a small amount of sodium hydroxide is added to the mixture. The small amount of sodium hydroxide added, apparently produces no material change in the nature of the clay, for  $x$ -ray diffraction patterns of the clay taken before and after such treatment, are identical.

The clay can be easily purified by agitation with water, settling, decanting, and filtering off the clay material remaining in suspension after the impurities have settled. Samples were purified in this way for chemical analysis and judging from the resultant analysis, all but 2.47% of the mineral impurities were removed from the clay.

The analysis by Mr. A. M. Smoot of Ledoux and Co., New York, is as follows:

	Per cent
SiO <sub>2</sub>	54.73
Al <sub>2</sub> O <sub>3</sub>	38.37
TiO <sub>2</sub>	1.35
Fe <sub>2</sub> O <sub>3</sub>	.40
CaO	.56
SO <sub>3</sub>	.16
H <sub>2</sub> O+110°	13.19
H <sub>2</sub> O-110°	.50
Total	100.26

Alkalies, magnesium and zirconium were absent.

The ratio of  $\text{Al}_2\text{O}_3:\text{SiO}_2$  according to the above analysis is 1:2.02 and the formula of the clay mineral would be:  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . Titanium oxide, ferric oxide, calcium oxide, and sulphur trioxide are probably due to the impurities not separated out during purification.

The samples of the clay examined were so finely crystalline that only a partial optical examination was possible. The indices of refraction were found to vary between the limits  $N_\alpha = 1.556$  ( $\pm .002$ ) and  $N_\gamma = 1.564$  ( $\pm .002$ ), with a corresponding double refraction of 0.006. The optical character is (—) and the acute bisectrix is nearly perpendicular to the perfect cleavage. The flakes show a very small angle of extinction.

The  $x$ -ray diffraction pattern has the same intensity variation, and computations show the same interplanar spacing as patterns of anauxite from Bilin, Bohemia, and from the Ione formation of California. The measurements and the results of the computations of interplanar spacings for the Brooklyn clay, agree within the limits of experimental error with the anauxite-kaolinite figures given by Ross and Kerr.<sup>15</sup>

#### VERMICULITE

Greenish mica, probably vermiculite, is prominent in the weathered zone. In general it is produced by the decay of the biotite in the granodiorite. In places, however, it may be observed undergoing alteration to kaolinite. It is variable in optical properties. Selected flakes yielded the following optical data:

$N_\alpha = 1.585$ ,  $N_\gamma = 1.593$  (approximately).

Double refraction, 0.008.

Wavy extinction, parallel in sections, normal to cleavage.

Pleochoric,  $X$ =green,  $Y$ =colorless,  $Z$ =pale yellow.

Biaxial (small angle).

Optically negative.

Chunks of flakes exfoliate upon heating with a blowpipe and the  $x$ -ray diffraction patterns closely resemble  $x$ -ray patterns of vermiculite, from Delaware Co., Pennsylvania, and do not agree with chlorite patterns taken in connection with previous investigations.

<sup>15</sup> *Op. cit.* Also Ross, Clarence S., and Kerr, Paul F., The minerals of kaolin: *Jour. Amer. Ceram. Soc.*, (In press).

## KAOLINIZATION

The feldspars are the first to undergo attack and replacement by kaolinite. An illustration of the attack upon a crystal of orthoclase is shown in Figure 7.

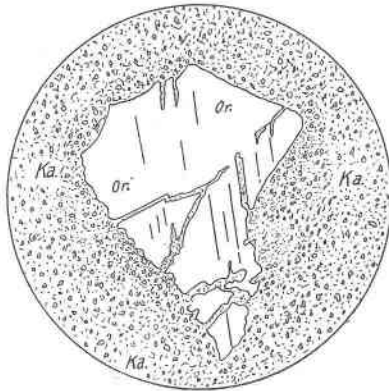


FIG. 7. Drawing of thin section  $\times 25$ . Orthoclase (Or) surrounded and in part replaced by kaolinite (Ka). Typical of the kaolinization of feldspar noted in thin sections.

The orthoclase section represents a single crystal as shown by simultaneous extinction throughout, yet it has been penetrated and cut in all directions with the resultant formation of kaolinite.

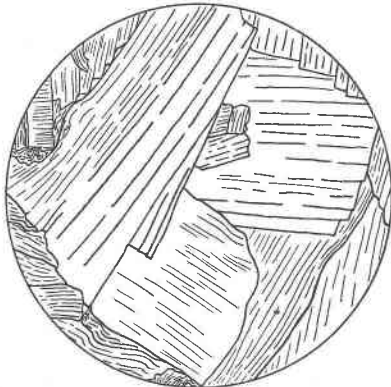


FIG. 8. Drawing of thin section  $\times 25$ . A mass of green vermiculite which, judging from color variations in adjacent areas, is an alteration of biotite.

Hornblende is shown in Figure 6 to be undergoing replacement by kaolinite. In this instance, however, intermediate replacement of hornblende by calcite is in evidence.

A change from biotite to kaolinite appears to take place in stages. Fig. 8 represents what may be considered the first stage and at the same time one of the most common throughout the rock. The biotite is altered to vermiculite without change in form. The vermiculite is prominent particularly in the weathered zone, and in instances, almost pure green masses are to be found. The vermiculite is so prominent that it might be considered to represent a different process of mineralization if it were not for numerous isolated occurrences in which nearly all gradational phases from biotite through vermiculite to kaolinite are to be seen. Fig. 9 illustrates a portion of this evidence. Sheaf-like structures re-



FIG. 9. Drawing of thin section  $\times 25$ . Remnant structures originally biotite but now kaolinite within a ground mass of kaolinite. The sheaf-like structure is apparently due to the marginal expansion of the mica flakes, during the replacement. The streaks are dark colored residual stains. (Indicated by the arrow.)

tain in part the original micaceous structure common to the biotite in the rock, yet are swollen on the margins. The margins are also largely kaolinite while the centers of the structures retain altered residual portions of the original mica.

Fig. 10 illustrates another way in which the replacement of biotite by kaolinite appears to take place. The mineral with well-defined cleavage shown in high relief is biotite. In parts of the figure it is still unaltered. In the center of the figure, appears a rope-like structure drawn to represent a gel-mineral (apparently amorphous). The gel-mineral is in places deep yellowish-brown in color, as if containing limonitic stain. Other portions, however are deep green and these in turn grade into extremely finely crys-

tallized kaolinite. It would appear from this sequence from biotite to kaolinite through the gel-minerals, that the iron and extra elements from the biotite are lost during the gel stage. A predominance of green color after the first stage in gel formation suggests that perhaps the iron present has been reduced and that the chemical reactions bringing the alterations about may be reducing

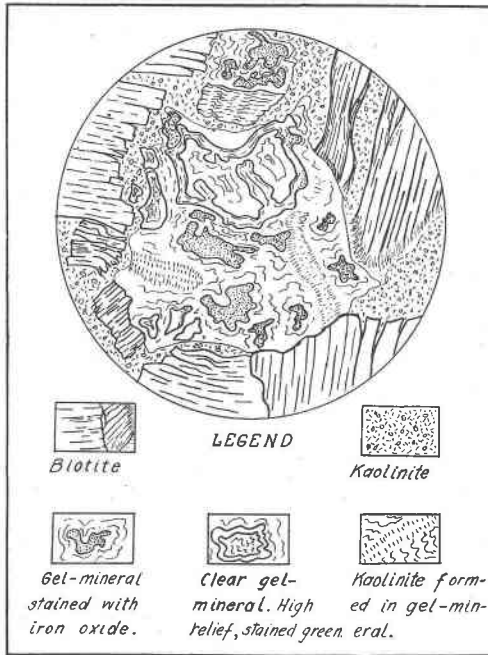


FIG. 10. Drawing of thin section  $\times 25$ . Progressive alteration in micaceous portion of the rock to form kaolinite. An isotropic brown gel-mineral is first produced which grades into a green gel-mineral phase. The latter grades in turn into a pale green gel-mineral which grades into kaolinite. The progressive loss of color and structure in the sequence of gel-minerals suggests reduction and removal of iron.

in character. Humphreys and Julien carried on no microscopic work but from their field observations, concluded that the rock decay was probably due to the corrosive action of organic acids acting in old peat-bogs. The character of the alterations observed in thin sections in no way refutes this hypothesis. In fact the production of a gel-like mineral and the subsequent crystalliza-

tion with removal of ferro-magnesian content might easily be brought about by the action of such acids.

The gel-minerals could not be isolated for identification but from the chemical nature of the end product allophane and halloysite may be judged to be present.

#### SUMMARY

A white clay discovered in a subway tunnel excavation near Newtown Creek, Long Island, is found to be kaolinite. It occurs beneath glacial till, as a weathering product of the Ravenswood granodiorite. It is associated with greenish less altered areas of weathered granodiorite containing vermiculite. The decay of the rock and the later formation of kaolinite were probably both produced by pre-glacial weathering.

The occurrence provides a description of a typical residual kaolin composed essentially of the mineral kaolinite as strictly defined. Emphasis is placed upon the necessity of careful identification in the case of kaolinite in order to distinguish the mineral from closely related species.