Trioctahedral minerals in the soil-clays of north-east Scotland.

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THIS paper deals with a series of soil-clay minerals which have a widespread distribution in the north-east of Scotland. The original member is a biotite-like mica which breaks down readily in the soil into (i) a vermiculite or (ii) a montmorillonite, depending on the soil-forming conditions operating. Apart from this 'clay biotite' and its decomposition products, the main crystalline constituents of the Scottish soil-clays are a member of the kaolinite group and illite ('clay muscovite'). Iron and aluminium oxides are present in all the clays in the amorphous condition, but crystalline varieties are scarce. The distribution of the minerals and their relationship to the various soil-forming factors will form the subject of a separate communication; here, the nature of the clay minerals and their interrelationships are considered.

Apparatus.

The present work has been carried out mainly by means of X-ray diffraction supplemented wherever possible by other methods. X-rays were generated from a continuously-evacuated self-stabilizing gas tube, Fe-$K\alpha$ radiation being used throughout because of the large amounts of iron present in the soil-clays and the consequent excitation of secondary radiation with primary copper radiation. The focus on the target was such that the maximum output of the tube was 37 kilovolts, 10 milliamps, if holing of the target face was to be avoided. With this arrangement, well-exposed powder photographs were obtained in 12–18 hours. 9-cm. cameras of a modified commercial type and similar to those described by MacEwan (1) were used and were evacuated to about 2 cm. Hg during operation. Adjustments made to the slits of the collimating systems ensured that diffractions up to 35 Å. could be measured. Back-scatter from the undeflected beam was prevented by fitting directly on to the back of the film at the exit hole a readily removable lead shield with a hole coincident with but of slightly smaller size than that in the film.

Nomenclature.

The terms trioctahedral and dioctahedral were proposed by Stevens (2), the former to designate layer minerals in which all possible octahedral positions are occupied and the latter for those in which one in three octahedral positions are vacant. As applied to the members of the mica group they are interchangeable with the better-known terms octophyllite and heptaphyllite (3) respectively. Outside the mica group, however, the terms are not necessarily equivalent, since talc and vermiculite, for example, are trioctahedral minerals although they are not octophyllites.

The difficulty of differentiating between the various micas by means of X-ray powder diffraction alone has been pointed out by Nagelschmidt (4). As he has shown, however, there are distinct differences between the muscovite and phlogopite-biotite type of powder diagram, that is to say, between the diagrams of dioctahedral (or heptaphyllite) and trioctahedral (octophyllite) micas. Perhaps the most important difference between the two groups lies in the position of a well-marked reflection which, in the dioctahedral members, always occurs at about 1·49–1·51 Å. and, in the trioctahedral types, at 1·53–1·55 Å. (We shall refer to this reflection for simplicity as the (060), although other sets of indices may also be assigned to it.)

From an examination of the powder diagrams of trioctahedral and dioctahedral minerals not of the mica group it appears that this relationship is a general one for layer-lattice silicates, which can be classed in most cases as trioctahedral or dioctahedral from the position of their (060) line (or (06) line, in the case of the 'two-dimensional' structures). The maximum range of position of this line in dioctahedral minerals is about 1·485–1·520 Å. and, in trioctahedral types, 1·515–1·560 Å. A (060) spacing greater than 1·52 Å. is thus a fairly definite indication of a trioctahedral mineral, and one less than 1·51 Å., of a dioctahedral type. Use is made of this relationship in the present paper in describing certain of the soil-clay minerals, which are classed as trioctahedral solely from the position of this line on the diffraction diagram, since reliable chemical data on the pure minerals are very difficult to obtain.

The trioctahedral mica.

X-ray photographs of Scottish soil-clays frequently show at about 1·53 Å. a medium to strong reflection forming a part of the diffraction pattern of a micaceous mineral or its decomposition products. Occasionally the associated first-order basal reflection at 10 Å. is sharp and

due to the presence of an unweathered mica; although more generally the reflection is diffuse, or it may be displaced to a different position, because of the readiness with which the 10 Å. mineral breaks down in the soil. The diffraction diagram of the unweathered mineral is given in table I. In its trioctahedral nature, this soil-clay mica differs from all the micaceous constituents of clays so far described which appear to be exclusively dioctahedral types.[1] From its powder pattern it would seem to bear the same relation structurally to biotite as dioctahedral illite does to muscovite (fig. 1).

TABLE I. X-ray diffraction diagram of the trioctahedral clay mica
(Fe-$K\alpha$).

dÅ.	$I_{est.}$	Indices.	dÅ.	$I_{est.}$	Indices.
10·0	10	002	2·41	4	133, 203
4·94	2	004	2·158	2	135, 205
4·47	9	020, 110	1·982	1	0010
3·68	2 b	113, 023	1·689 }	3	0012 &c.
3·32	9	006	1·649 }		
3·16	0·5	114	1·530	6	060, 330
2·86	1	115	1·446	0·5	
2·60	6	200, 13$\bar{1}$	1·320	0·5	400
2·50	1	008			

b = broad.

The name *illite* was proposed in 1937 by Grim, Bray, and Bradley (5) as a group name for all the micaceous constituents of clays, with the reservation that it might be desirable at some future date to re-define the term so as to restrict it to a particular type of clay mica. So far, the term has been applied to micas of the muscovite type only, and it may eventually be found convenient to use illite in this sense alone, in which case the term could not be applied to the trioctahedral clay mica. On the other hand, if illite is to be adopted as a group name for all clay micas, then the trioctahedral mica of the Scottish soil-clays would be classed as a *trioctahedral illite*. In view of the present indefinite meaning of the term illite, the soil-clay mica will be referred to in the present communication as the *trioctahedral clay mica* or simply as 'clay biotite'.

The possibility has been considered that the name *pholidolite* might be used, since Hendricks (6) has suggested that this mineral might be the degraded trioctahedral mica equivalent to the dioctahedral illite. Pholidolite, however, is an imperfectly defined mineral described by

[1] Recently MacEwan (1) has noted the existence of a trioctahedral mica in certain Scottish soil-clays.

Nordenskiöld (7) found only in drusy cavities in certain Swedish rocks, and is not essentially a clay mineral.[1] Similarly, the name *biotite* cannot be justifiably applied to the clay mineral for the same reasons as those which led Grim, Bray, and Bradley (5) to reject muscovite as a name for the dioctahedral clay mica. Thus, the manner of occurrence of the Scottish mineral, for example, suggests that it is not formed simply by the mechanical disintegration of ordinary biotite (see below). In spite
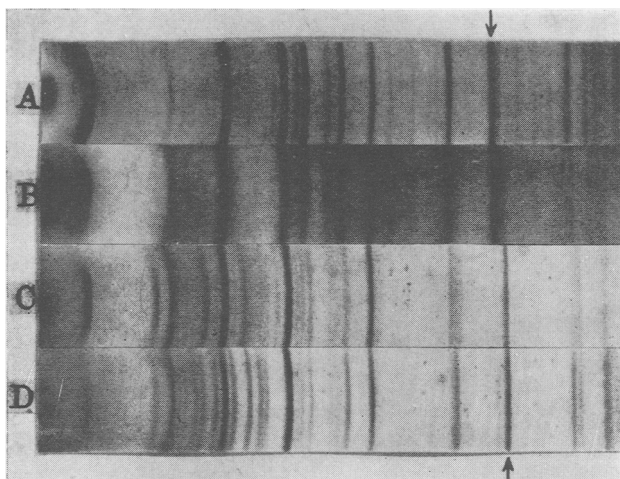

FIG. 1. X-ray powder diffraction photographs of: Å, biotite, Glen Buchat, Aberdeenshire; B, the trioctahedral clay mica, Balquhain, Aberdeenshire (this clay was heated at 700° C. to eliminate kaolinite lines); C, dioctahedral illite, Ballater, Aberdeenshire; D, muscovite, Goshen, Massachusetts. (Arrows indicate positions of (060) lines.)

of these difficulties, however, it is not proposed to introduce a new mineral name at this time, since it is felt that this would be likely merely to add to the existing confusion in the nomenclature of the clay micas, especially since data on the trioctahedral clay mica itself are still rather scanty.

[1] Through the kindness of Professor Sven Gavelin of Stockholm and Dr. B. Collini of Uppsala I have been able to take X-ray powder photographs of a sample of Nordenskiöld's material from Taberg, Sweden. Although it has the appearance of an altered mica this material gives the powder pattern of a trioctahedral montmorillonite, indicating that it consists of an aggregate of montmorillonite crystallites pseudomorphous after mica. The degree of alteration of Nordenskiöld's material, however, probably varies in different parts of his samples since his optical and chemical data suggest that the material which he himself examined may have been less highly altered than the sample examined by the present writer.

The weathering of the trioctahedral mica.

(a) *The vermiculitic product.*—X-ray photographs of the soil-clays show the 'clay biotite' in various stages of decomposition, but seldom in the unweathered condition. Out of some hundreds of soil-clays examined it occurs fresh in only a few cases and then at the bottoms of the profiles in the relatively unweathered parent material horizons. More normally, it occurs as a mixed-layer structure with vermiculite to which it breaks down readily under a wide range of conditions, the process of breakdown approximating to the breakdown of macroscopic biotite into vermiculite in the sand fractions of the soil (8). In many cases, the process of decomposition can be traced upwards through successive layers of the profiles, from the unweathered or nearly un-weathered condition of the mineral at the bottom of the profile to its vermiculitic weathering product in the surface layers. The process is best followed in a virgin profile which has not been subjected to cultiva-tion.

Initially, the decomposition process is seen as a broadening of the first-order basal reflection at 10 Å., and in some photographs a tendency for this reflection to tail off on the low-angle side is observed. The intermediate stages of the process are characterized by the presence of diffraction bands stretching from 10 Å. to 14 Å. on the photographs and corresponding to varying numbers of 10 Å. and 14 Å. mixed layers. Sometimes the bands are of uniform intensity and have well-defined edges; more commonly they consist of two diffuse peaks at 10 Å. and 14 Å. with a region of minimum intensity between. Nowhere has there been found a single reflection at 11·5 Å. or 12 Å. such as occurs in hydrobiotite, the mixed-layer mineral described by Gruner (9) which consists of approximately equal numbers of mica and vermiculite layers.

The 14 Å. reflection of these clays is not displaced to 17·7 Å. on treatment with glycerol (10) so that it cannot be due to montmorillonite; and its replacement by a line at 9–10 Å. after heating at 500° C. for a number of hours indicates that the 14 Å. mineral is a vermiculite rather than a chlorite. The displacement of the 14 Å. reflection to 10·5 Å. on saturating the clay with ammonium ions confirms the identi-fication, since this reaction is found to occur with vermiculites but not with chlorites (11, 12). It is plain that these soil-clays do not contain appreciable amounts of chlorite, but the possibility of the presence of relatively small numbers of chlorite layers occurring interleaved with vermiculite layers cannot be dismissed.

As in the weathering of macroscopic biotite (8), the weathering process of the trioctahedral clay mica consists first of all in the loosening of the attractive forces binding the 10 Å. mica layers together, followed by the taking-up of double layers of water molecules between each pair of alumino-silicate layers. When this process is complete the mineral is a vermiculite and gives a strong (002) reflection at 14 Å. (table II).

TABLE II. X-ray diffraction diagrams of the weathering products of the trioctahedral clay mica (Fe-$K\alpha$).

1.		2.	
dÅ.	$I_{est.}$	dÅ.	$I_{est.}$
14·1	10	17·8	10 b
4·9	2	9·0	3 d
4·59	2	4·56 ⎫	5 d
3·51	4	4·20 ⎭	
3·18	1	3·66	2
2·93	1	3·0	1 d
2·71	1	2·56	4 d
2·63	4	2·44	4
2·44	4	1·70	0·5
1·530	6	1·532	5
1·32 ⎫	2 d	1·31	1 d
1·28 ⎭			

b = broad; d = diffuse.

1. Vermiculitic product.
2. Montmorillonitic product (glycerol-saturated).

In the decomposition of macroscopic biotite into vermiculite a certain stage occurs at which a *single* layer of glycerol molecules can be introduced between the alumino-silicate layers causing the expansion of the lattice from 10 Å. to 14 Å. to take place prematurely (8), and the same reaction is found to occur during the decomposition of the 'clay biotite'. In most of the soil-clays partially decomposed (and potentially-expanding) layers of the 'clay biotite' as well as unweathered layers and vermiculite layers exist together, so that the addition of glycerol to the clay usually causes the expansion of a proportion of the 10 Å. layers. This is seen on the diffraction photographs as an enhancement of the 14 Å. reflection relative to the 10 Å. if separate 10 Å. and 14 Å. reflections were originally present (fig. 2 B); or if a band of more or less uniform intensity was present at 10–14 Å. before treatment, the intensity in the 14 Å. region becomes relatively stronger and a sharp 14 Å. reflection may be resolved (fig. 2 c). In the early stages of decomposition, there may be no 14 Å. line perceptible till after glycerol saturation (fig. 2 A); on the other hand, at a sufficiently advanced stage of decomposition all the layers will have expanded to 14 Å. by natural means,

and in this event addition of glycerol causes no further change (fig. 2 D).

(b) *The montmorillonitic product.*—Although the weathering product of the 'clay biotite' is normally a vermiculite, under certain conditions
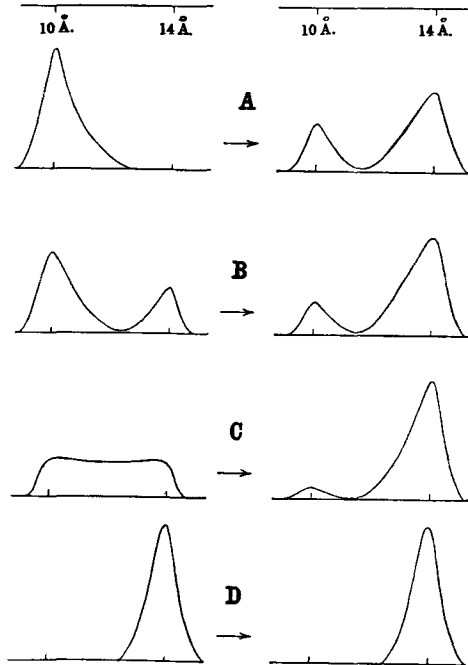

FIG. 2. The effect of glycerol treatment on the shapes of the 10 Å. and 14 Å. reflections at various stages during the breakdown of the trioctahedral clay mica into vermiculite (diagrammatic).
  A. Glycerol treatment causes a 14 Å. reflection to develop with a corresponding reduction in the intensity of the 10 Å. reflection.
  B. The intensity of the 14 Å. reflection increases relative to that of the 10 Å. after treatment.
  C. A sharp 14 Å. reflection is resolved from a 10–14 Å. band by the treatment.
  D. An already fully-developed 14 Å. reflection is unaffected by treatment.

the breakdown proceeds directly to the formation of a trioctahedral mineral with a freely-expanding lattice like montmorillonite.[1] Two conditions seem to be necessary for the formation of this product, since it occurs only in soils: (i) derived ultimately from basic or ultra-basic rocks; and (ii) under poor drainage conditions, that is, where the soil

[1] The diffraction pattern of this material resembles that of the sample of Nordenskiöld's pholidolite examined by the writer.

remains below the level of the water-table for long periods of the year. Saturation of this mineral with glycerol leads to the taking-up of a double layer of glycerol molecules giving the strong 17·7 Å. reflection typical of glycerol-montmorillonite (10) (table II). In its natural state the mineral gives a diffraction pattern showing a weak and indefinite band at 10–16 Å. or thereabouts in place of a sharp basal reflection, suggesting pronounced variation in the numbers of water layers between successive alumino-silicate layers. In appearance this slight hazing of the photograph is quite unlike the relatively well-defined 10–14 Å. band which forms during the alteration of the 'clay biotite' into vermiculite, and its reaction to glycerol treatment is also quite distinct.

Both the conditions mentioned above appear to be necessary for the development of the montmorillonitic product of weathering; if only one holds, the weathering product is vermiculite. Thus, vermiculite forms from the 'clay biotite' in soils of intermediate or acid origin irrespective of the drainage conditions, and also in the more freely-drained soils of basic origin. In certain basic soils where the lower layers are more or less normally waterlogged while nearer the profile surface freer drainage conditions exist, the montmorillonitic weathering product present in the lower layers gives way to the vermiculitic product in the surface layers, and both may coexist in the intermediate layers.

(c) *Rate of breakdown.*—The rate at which the trioctahedral clay mica breaks down in the soil is a notable feature. As has been already indicated, considerable searching was required before a clay was found which gave a single sharp basal reflection at 10 Å. which was not affected by glycerol treatment. Compared with its dioctahedral analogue illite, the trioctahedral mineral decomposes rapidly, although Nagelschmidt (13) has suggested that the former mineral is also unstable under humid temperate conditions. According to Nagelschmidt, as illite alters, the 10 Å. reflection tends to form a 'tail' extending towards low angles and the first well-defined product of its breakdown is a montmorillonite, a process of breakdown very similar to that found with the trioctahedral clay mica under the special circumstances defined above. On the other hand, no parallel to the more usual breakdown of the trioctahedral mineral into vermiculite with its comparatively definite steps seems to occur with the dioctahedral clay mica.

The removal of free oxides from the clays.

When examining soil-clays by X-ray methods it is often advantageous to remove the free iron and aluminium oxides which form amorphous

coatings round the crystalline particles and cause general scattering of the X-ray beam, and several excellent methods of achieving this are available. It is advisable, however, to use such chemical treatments with care since they may lead to misinterpretations if the clays concerned are vermiculite-bearing. The replacement of the exchangeable magnesium ions which are normally present in vermiculite by other ions has been shown to cause changes in the structure of the water layers and hence in the position of the basal reflections on the diffraction photographs (11, 14). Thus, if an iron-removal treatment involving (say) an ammonium salt is used, the basal spacing of any vermiculite layers present may be wholly or partly displaced to about 10·5 Å. It is important, therefore, to determine the effect of such chemical treatments on the positions of the basal lines of a pure specimen of vermiculite before employing them on soil-clays suspected of containing vermiculitic minerals.

Chemical and cation-exchange data.

So far it has not been possible to isolate the 'clay biotite' or its weathering products from each other or from the kaolinite with which they are associated in the soil-clays,[1] and until this is effected detailed optical examination of the minerals must be foregone (15). For the same reason chemical and cation-exchange determinations on the pure minerals cannot be made directly. Another difficulty lies in the readiness with which the 'clay biotite' decomposes in the soil, a factor which at present makes it extremely difficult to decide whether the mineral is completely fresh in a given sample.

An attempt has been made to determine the approximate composition of the 'clay biotite' by recalculating the analysis of a clay in which the 10 Å. reflection is comparatively strong and sharp and unaffected by glycerol treatment, indicating that the mineral is in a fresh or fairly fresh condition. It has been shown, however, that during decomposition in the soil the chemical composition of ordinary biotite alters considerably before much change is observed on the X-ray diagram (8), and it is probably correct to assume that this is also true of the clay mineral. The presence of a 10 Å. reflection is therefore no guarantee that the mineral has not altered chemically to some extent, and the

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[1] X-ray photographs of clay sub-fractions separated by means of the supercentrifuge failed to reveal any pronounced tendency for the trioctahedral minerals to concentrate in a particular size fraction.

low alkali and very high water contents obtained (table III) suggest that it has in fact done so.

TABLE III. Chemical analysis (recalculated to allow for impurities) and atomic composition of the trioctahedral clay mica (calculated on the basis of OH = 8, O = 40).

SiO_2	... ...	40·87	Si	13·20	}	16
Al_2O_3	... ...	20·45	Al	2·80		
			Al	4·97		
TiO_2...	... ...	2·13	Ti	0·53		
Fe_2O_3	... ...	12·81	Fe^{+3}	3·06	}	11·89
MgO	... ...	6·86	Mg	3·26		
MnO	... ...	0·25	Mn	0·07		
CaO	... ...	0·89	Ca	0·31		
K_2O	... ...	3·25	K	1·33	}	2·05
Na_2O	... ...	0·70	Na	0·41		
$H_2O+(105-300°$ C.)		4·94	OH	8	}	48
$H_2O+(300°$ C.)	...	6·90	O	40		

100·05

Comparison with standard X-ray photographs of artificial mixtures of mica and kaolinite indicates that 35 % ($\pm$5 %) kaolinite is present in the analysed clay, and the figures in table III have been arrived at after allowing for this amount. Treatment of the clay with sodium hydrosulphite (16) extracted 7·50 % 'free' Fe_2O_3, and this has also been taken into account; amorphous alumina and silica, on the other hand, were negligibly small. The amounts of water released on heating at 105° C. and at 300° C. were determined after removal of the free iron oxides. The proportion of water and hydroxyl actually associated with the trioctahedral mica is, however, uncertain, and the atomic composition given in table III has therefore been calculated on the basis of OH = 8, O = 40. The percentage of ferrous iron is also unknown since the small amount of organic matter remaining in the soil-clay even after repeated peroxide treatments interfered with its determination.

In view of the foregoing it is clear that the analysis quoted in table III may be regarded at best as no more than a rough approximation to the true composition of the trioctahedral clay mica. It has been included here simply because anything closer than a rough approximation will be difficult to obtain until a method of isolating the mineral is available. It is clearly essential to keep the limitations of the analysis in mind in any comparison with other mineral analyses.

The cation-exchange capacity of the analysed clay was determined after removal of the free iron oxides. After making allowance for the kaolinite constituent and neglecting the effect of the inorganic amor-

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phous component, the exchange capacity of the 'clay biotite' is found to be about 40–50 m. equiv. per 100 g. of clay, although it is possible that a somewhat lower value would be obtained if the mineral was completely fresh. Similar determinations on the vermiculitic and mont-morillonitic products of weathering indicated an exchange capacity in the region of 100 m. equiv. per 100 g. in both cases.

Field relations.

The soils of the area belong to the Large Podzol Zone and are in the main members of the Grey-Brown and Brown Podzolic Sub-zones (17). They are developed on glacial drift laid down some 10,000–20,000 years ago, and although there has been a certain amount of mixing of parent-material types, in general the soil-types are clearly distinguishable in the field. Soil-clays from a wide range of parent-material groups have been surveyed including parent materials ultimately derived from acidic, intermediate, basic, and ultrabasic igneous rocks, from quartzose- and mica-schists, slates, mudstones, sands, and gravels, and red clay.

In the clay fractions of these soils the trioctahedral clay mica and its weathering products are widespread and frequently make up half or more of the crystalline component. The amounts of these minerals in the clays appear to bear no relation whatsoever to the amount of biotite in the rocks from which they are derived; and it is, as a consequence, improbable that the 'clay biotite' is a residual mineral produced by the disintegration and degradation of the original biotites of the parent rock, but rather that it is formed as an authigenic mineral in the soil-clays. The presence of the 'clay biotite' itself in the clay fraction of a given soil is, moreover, not incompatible with the coexistence of vermiculite flakes in the sand fraction of that soil, the latter material having been formed by the decomposition of macroscopic biotite.

The weathering changes in the trioctahedral clay mica are easily followed on the diffraction photographs from the positions and shapes of the basal reflections. The initial identification of the mineral and its decomposition products is, however, not always straightforward in the presence of other clay minerals. Thus, the important (060) line (or (06) line in the case of the montmorillonitic member) of the trioctahedral minerals coincides with a quartz line at 1·53 Å. so that the presence of quartz is a distinct hindrance to their identification. If this mineral is present, comparison of the relative intensity of the 1·53 Å. line with the 1·81 Å. and 1·37 Å. lines of quartz which are of the same intensity may indicate whether the first of these lines is wholly due to the quartz

or not; but the exclusion of quartz from the sample by selecting a finer size fraction may be necessary. The majority of the soil-clays examined during this investigation show no sign of quartz in the fraction $< 1 \cdot 4\,\mu$ equivalent spherical diameter, and even in those clays derived from quartz-bearing rocks the amount of quartz present is either negligible or very small in this size fraction, so that at most only the strongest quartz line at 3·35 Å. is visible on the diffraction photographs.

In several of the soil-clays, dioctahedral illite coexists along with the trioctahedral minerals and kaolinite, and at one locality in Aberdeen-shire (Ordley) it makes up 70 or 80 % of the crystalline material, the other 20–30 % consisting of kaolinite and haematite. With this single exception all the localities in the north-east of Scotland examined so far have shown evidence of appreciable amounts of the 'clay biotite' and/or its weathering products. It is interesting to note that we have also found minerals of this type in soil-clays from the south and west of Scotland, and from Northern Ireland.

In conclusion, it may be noted that the difficulty of distinguishing the 'clay biotite' from its dioctahedral analogue by means of X-rays in the presence of other clay minerals and quartz suggests the possibility that the two micas may have been confused in the past. Similarly, the distinction between vermiculite and montmorillonite is a fine one and, before the glycerol method for the positive identification of the latter mineral (10) was developed, it is probable that it was not always made, since the usual heating test quoted in the literature for confirming the presence of montmorillonite would not eliminate vermiculite (viz. dis-placement of the 14 Å. line to 10 Å. after heating the sample at 500° C. for several hours). The high cation-exchange capacity possessed by vermiculite and unsuspected until recently (14) would also tend to cause its confusion with montmorillonite.

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