

# SOME HYDROUS MICAS IN SOUTH AFRICAN CLAYS AND SHALES

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At the 4th International Soil Science Congress held in Amsterdam (1950) a special meeting discussed the nomenclature of clay minerals and suggested "hydrous mica" as a general term for those clay minerals that are neither well crystallised micas nor pure expanding minerals.

In the past various names have been used for the hydrous micas. As early as 1912, Galpin, and later, in 1920, Bayley, introduced the terms "hydro-mica" and "hydrous mica" respectively, to designate a micaceous clay mineral. Since then, reports have been made of the presence in soils of a potash-bearing clay mineral (Wherry *et al.*, 1929), and in clays of a mica-like clay mineral (glimmerartige Tonmineralien) (Endell *et al.*, 1935), and a sericite-like mineral (Grim, 1935). In 1937 Grim *et al.*, for the first time proposed the term "illite" as a "general term for the clay mineral constituents of argillaceous sediments belonging to the mica group." Other names include bravaisite (Ross and Hendricks) and sarospatite (Maegdefrau and Hofmann, 1937), but the validity of these as specific minerals is questionable since they have been found to exist as mixtures of hydrous micas and montmorillonoids (Bradley, 1945; Brindley, 1951).

Generally speaking, the modern concept of the term "hydrous mica" seems to describe the clay minerals that contain less potash and more water than the well crystallised micas. Included under the hydrous micas are the illites and the mixed-layer minerals, where the general term "illite" indicates those clay micas which show no significant swelling of the basal 10 Å X-ray reflection.

More data, and the definite elimination of the possibility of mixed-layer minerals in reported minerals like brammallite (Bannister, 1943) and Al- and Mg-illidromica (Andreatta, 1949) is necessary to determine their validity and position in the mica-hydrous mica-montmorillonoid series.

From clays and shales investigated at the National Chemical Research Laboratory examples have been chosen where the identified clay mineral proved to be a hydrous mica and representative of the mica-montmorillonoid sequence, *i.e.*: (a) a hydromuscovite; (b) an illite; (c) two random mixed-layer minerals; and (d) a regular mixed-layer mineral.

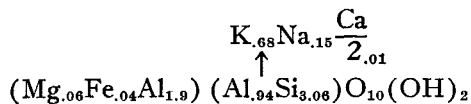
The occurrence of hydrous mica clay minerals in South African soils will be discussed in a separate paper.

## A. HYDROMUSCOVITE

According to the terminology proposed by the 4th International Soil Science Congress, the mineral hydromuscovite described by Brammall *et al.* (1937) should be classified as an illite although as regards its chemical composition (Table I) and perfection of crystallinity it seems to lie between muscovite and illite, that is, if we take the data reported for the Fithian illite by Grim *et al.* (1937) as typical for illites.

The material collected near Pretoria (at the upper contact of Ongeluk lava with Pretoria shale, Lynnwood Township) should also be classified as a hydromuscovite because its chemical analyses (Table I) and X-ray diffraction values (Table II) compare very well with that reported by Brammall and co-workers for the hydromuscovite from Ogofau, Wales. As already mentioned, the main differences between this mineral and a typical illite are an apparently better crystallinity (Table II), a higher content of K<sub>2</sub>O and less water (Table I).

The following formula was calculated from this chemical analysis:



Additional data obtained for the hydromuscovite occurring locally indicated other marked differences from typical illite, and these support the inclusion of the term hydromuscovite as a mineral name in the hydrous mica group. The ion exchange capacity of the hydromuscovite is about 2.5 m.e./

TABLE I

	Chemical analyses of:			
	Muscovite <sup>1</sup>	Hydro- muscovite <sup>2</sup>	Hydro- muscovite <sup>3</sup> Pretoria	Illite <sup>4</sup>
SiO <sub>2</sub>	44.85	46.54	46.37	51.22
Al <sub>2</sub> O <sub>3</sub>	36.95	36.37	36.51	25.90
Fe <sub>2</sub> O <sub>3</sub>	1.54	0.72	0.96	4.59
FeO	1.36	0.36	—	1.70
TiO <sub>2</sub>	tr.	0.17	1.55	0.53
CaO	—	0.22	0.30	0.16
MgO	—	0.50	0.62	2.84
K <sub>2</sub> O	9.13	8.06	8.04	6.09
Na <sub>2</sub> O	1.78	0.46	1.16	0.53
Loss ign.	4.08	6.31	4.89	7.14
	99.69	99.71	100.40	100.70

<sup>1</sup> Jakob, J., *Zeits. Krist.*, 62, 443 (1925).

<sup>2</sup> Brammall, A., Leech, J. G. C., and Bannister, F. A., *Min. Mag.*, 24, 516 (1937).

<sup>3</sup> Rethemeyer, R., National Chemical Research Laboratory, Pretoria.

<sup>4</sup> Grim, R. E., Bray, R. H., and Bradley, W. F., *Amer. Min.*, 22, 823 (1937).

TABLE II. — X-RAY DIFFRACTION VALUES IN ANGSTROM UNITS<sup>1</sup>

Hydromuscovite (Brammell <i>et al.</i> , 1937)		Hydromuscovite Pretoria		Illite (Grim <i>et al.</i> , 1937)	
d.	Int.	d.	Int.	d.	Int.
9.98	s	10.0	vs	9.98	s
5.02	s	5.0	s	4.97	w
4.51	m	4.46	s	4.47	s
—	—	4.28	w	—	—
—	—	4.13	w	4.11	vw
—	—	3.86	m	—	—
3.62	s	3.72	m	3.7	vw
—	—	3.48	m	3.4	vw
3.34	vs	3.34	vs	3.31	m
3.09	s	3.19	ms	3.2	vw
—	—	2.987	ms	2.98	w
2.89	s	2.860	m	2.84	vw
—	—	2.789	m	—	—
2.59	vs	2.578	m	2.56	s
—	—	2.544	s	—	—
—	—	2.501	w	—	—
2.470	m	2.452	m	2.44	w
2.390	s	2.376	m	2.38	m
2.27	}w{	—	—	2.24	m
2.18		—	—	2.18	w
2.135	s	2.143	m	—	—
—	—	2.126	m	2.11	w
1.994	vs	1.997	m	1.98	m
—	—	1.972	w	—	—
1.715	vw	1.725	w	—	—
1.648	s	1.644	m	1.65	w
—	—	1.595	w	1.64	m
—	—	1.555	w	—	—
—	—	1.521	w	—	—
1.505	s	1.496	m	1.50	s

<sup>1</sup> vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

100 gm. of dried material, a very low figure compared to the values of 20-40 m.e. usually reported for illites. The d.t.a. curve is also quite unlike the typical curve for illites (Fig. 1). The d.t.a. curve for hydromuscovite shows one endothermic reaction at 720° C whereas that for muscovite takes place at 900° C (Carr *et al.*, 1953). For a fine-grained muscovite Grim (Brindley, 1951, p. 147) reported a curve similar to that of hydromuscovite.

Shannon (1926) described sericite as a mineral differing from muscovite by containing less potash and more water. It does not seem desirable to classify the above-mentioned mineral as a sericite because of the looseness of this term. It has been used for material essentially the same as fine-grained muscovite (List, 1852) for an alteration product of feldspar (Laspéyres, 1879), and for a low temperature hydrothermal mineral (Rogers, 1916). Such diverse use has naturally led to confusion and under the cir-

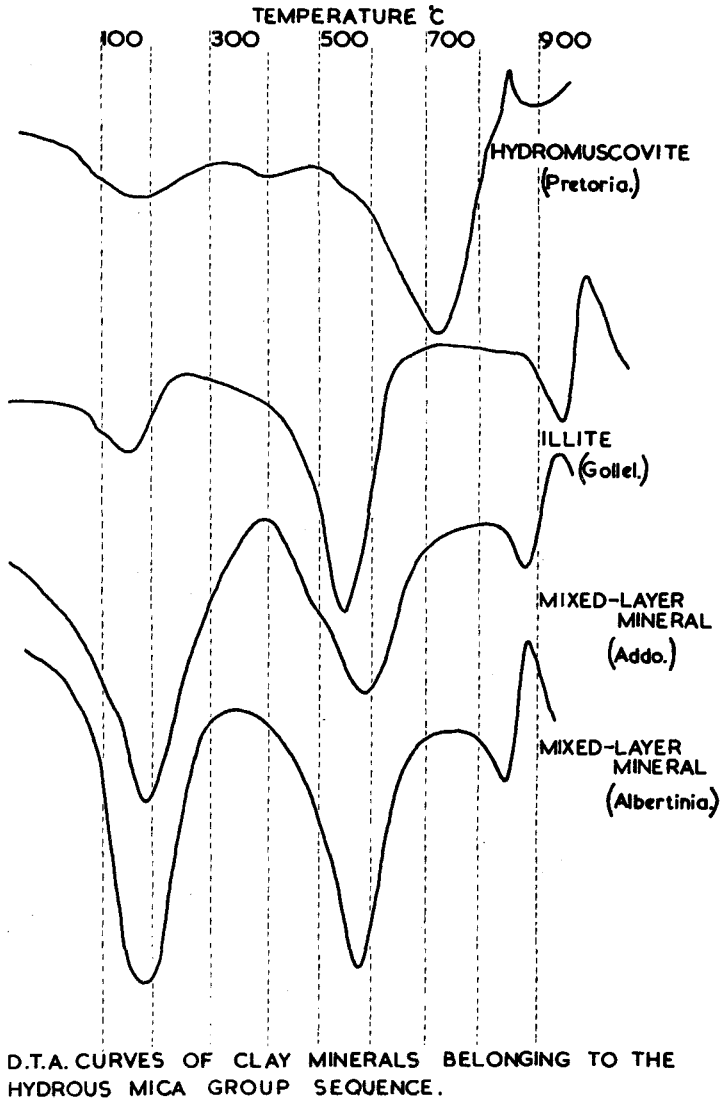


FIGURE 1

cumstances the author prefers to call the mineral under discussion a hydromuscovite.

### B. ILLITE

The chemical analysis of the mica clay mineral fraction of the clay from Gollel, Swaziland, compares well with that of various illites reported in the literature (Table III).

TABLE III. — CHEMICAL ANALYSES OF VARIOUS ILLITES

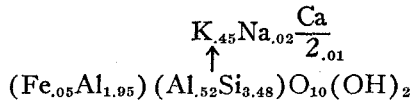
	Illite Fithian <sup>1</sup>	Illite Ballater <sup>2</sup>	Illite South Wales <sup>3</sup>	Hydrous Mica Yorkshire <sup>4</sup>	Illite Gollel <sup>5</sup>
SiO <sub>2</sub>	51.22	51.26	47.55	46.75	53.13
Al <sub>2</sub> O <sub>3</sub>	25.90	30.15	32.45	32.43	31.99
Fe <sub>2</sub> O <sub>3</sub>	4.59	2.36	0.76	2.98	1.18
FeO	1.70	0.59	1.85	n.d.	n.d.
TiO <sub>2</sub>	0.53	0.05	0.64	1.15	0.85
CaO	0.16	—	0.06	1.04	0.17
MgO	2.84	1.37	1.70	1.00	—
K <sub>2</sub> O	6.09	7.77	6.22	5.72	5.35
Na <sub>2</sub> O	0.53	0.13	1.05	0.94	0.18
Loss ign.	7.14	6.28	7.73	8.01	7.55
	100.70	99.96	100.01	100.02	100.40
Ion exchange capacity m.e./100 gm.	35.5				20.70

<sup>1</sup> Grim, R. E., Bray, R. H., and Bradley, W. F., *Amer. Min.*, 22, 823 (1937).  
<sup>2</sup> Mackenzie, R. C., Walker, G. F., and Hart, R., *Min. Mag.*, 28, 708 (1949).  
<sup>3</sup> Nagelschmidt, G., and Hicks, D., *Min. Mag.*, 26, 300 (1943).  
<sup>4</sup> Carr, K., Grimshaw, R. W., and Roberts, A. L., *Min. Mag.*, 30, 141 (1953).  
<sup>5</sup> Rethemeyer, R., National Chemical Research Laboratory, Pretoria.

The hydrous mica described by Carr *et al.* (1953) should rather be classified as an illite judging by its chemical analysis and d.t.a. characteristics. This d.t.a. curve is typical of that for illites, as is also the case with the curve of the clay mineral from Gollel (Fig. 1) where endothermal peaks occur at 150° C, 560° C and 950° C and an exothermal reaction at 990° C.

The illite from Gollel had an ion exchange capacity of 20.7 m.e. per 100 gm. of clay dried at 110° C, and this value falls within the range of ion exchange values typical of the illites.

From the chemical analysis the following formula was calculated:



The X-ray diffraction data (Table IV) compare well with those of the illite investigated by Grim *et al.* (1937), and as the basal 10 Å reflection shows no significant change when the mineral is subjected to mild thermal or chemical treatment, there is no doubt that this particular clay mica mineral should be classified as an illite.

When comparing the d-values (Table IV) of the illite with those of hydromuscovite, it is quite noticeable that the hkl reflections of the former are weak or absent as a result of its poorer crystallinity. In turn, this hydromuscovite has a lower perfection of crystallinity than a muscovite mica.

TABLE IV. — X-RAY DIFFRACTION VALUES IN ANGSTROM UNITS<sup>1</sup>

Hydromuscovite Pretoria		Illite (Grim, 1937)		Illite Gollel	
d.	Int.	d.	Int.	d.	Int.
10.0	vs	9.98	s	10.26	vs
5.0	s	4.97	w	5.04	m
4.46	s	4.47	s	4.47	m
4.28	w	—	—	4.30	w
4.13	w	4.11	vw	—	—
3.86	m	—	—	—	—
3.72	m	3.7	vw	3.69	w
3.48	m	3.4	vw	—	—
3.34	vs	3.31	m	3.33	s
3.19	ms	3.2	vw	—	—
2.987	ms	2.98	w	3.01	m
2.860	m	2.84	vw	—	—
2.789	m	—	—	—	—
2.578	m	2.56	s	2.57	m
2.544	s	—	—	—	—
2.501	w	—	—	—	—
2.452	m	2.44	w	2.43	w
2.376	m	2.38	m	2.379	w
—	—	2.24	m	2.244	w
—	—	2.18	w	2.206	w
2.143	m	—	—	—	—
2.126	m	2.11	w	2.132	w
1.997	m	1.98	m	2.011	m
1.972	w	—	—	—	—
1.725	w	—	—	—	—
1.644	m	1.65	w	1.653	br
1.595	w	1.64	m	—	—
1.555	w	—	—	—	—
1.521	w	—	—	—	—
1.496	m	1.50	s	1.502	m

<sup>1</sup> vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad.

### C. TWO RANDOM MIXED-LAYER CLAY MINERALS

Many clays consist of mixtures in which discrete and independent particles of the individual minerals occur. Another type of "mixing," however, first reported by Gruner in 1934, is the interstratification of parallel layers of separate minerals. In recent years such "mixed-layer minerals" have frequently been reported (Hendricks and Jefferson, 1938; Nagelschmidt, 1944; and MacEwan, 1949), and according to Grim (1953) mixed-layer minerals are apparently common in deposits of hydrothermal origin.

As techniques of X-ray diffraction of clay minerals improved, many previously described mineral species must now be considered as redundant as these clays were found to be mixed-layer minerals. Bravaisite (Ross and Hendricks) has been reported to be a random mixed-layer interstratification of about equal quantities of illite and montmorillonite (Bradley, 1945).

Similar results have been reported on sarospatite (Brindley, 1951). Beidelite (Larsen and Wherry, 1925) and Ordovician meta-bentonite (Ross, 1928), originally classified in the montmorillonoid group, are now also known to be random mixed-layer minerals. The Ordovician meta-bentonite was found to consist of 80 percent of nonexpandable layers (illite) and 20 percent of layers that were expanded (a montmorillonoid) (Weaver, 1953).

The random mixed-layer structures are now generally accepted as a separate type in the hydrous mica group. Their occurrence is common and they exist as random interstratifications of hydrous mica layers with montmorillonoid or vermiculite layers.

Both the random mixed-layer clay minerals discussed in this section came from the Cape Province, namely, near Addo and Albertinia respectively.

#### *Addo Shale*

The greenish grey shale from near Addo station belongs to the Bokkeveld Series and was collected at a depth of 6 feet below the surface. This material was crushed and through fractional sedimentation the colloidal fraction (particles less than 2 microns in size) was collected for mineralogical determination.

#### *Clay Mineralogy of the Addo Shale*

An X-ray investigation of the minus two micron fraction of the Bokkeveld shale near Addo proved the clay minerals to be kaolinite, montmorillonite and a hydrous mica.

This colloidal fraction was further separated with the Sharples super-centrifuge into fractions of 0.5-2 micron, 0.2-0.5 micron, 0.05-0.2 micron and <0.05 micron. The X-ray diffraction diagrams of the basal peaks of oriented samples of the three size fractions mentioned last are reproduced in Figure 2. Kaolinite was still present in the 0.2-0.05 micron fraction, but the <0.05 micron material only contained a hydrous mica as shown by the basal diffraction peak at 10.47 Å. This spacing is significantly greater than the 10 Å spacing expected of illite, and can be taken as an indication of interlayering, presumably with montmorillonite layers of 15.4 Å. The marked gradual increase in the intensity of the diffraction pattern in the direction of smaller angles is also characteristic of mixed-layer minerals (Brown and MacEwan, 1950). A mixture is out of the question, since a single peak is obtained instead of two peaks.

It would be expected that, if montmorillonite layers are present, a shift in the basal spacing will take place on treatment with glycol. That this occurred in the <0.05 micron fraction may be regarded as evidence of montmorillonite layers, but, instead of a single shift, the 10.47 Å peak split into a 10.0 Å peak and a weak 20.0 Å peak. The meaning of this requires some consideration.

The mathematical theory of X-ray diffraction for random mixed-layer structures was presented by Hendricks and Teller (1942) and a number of

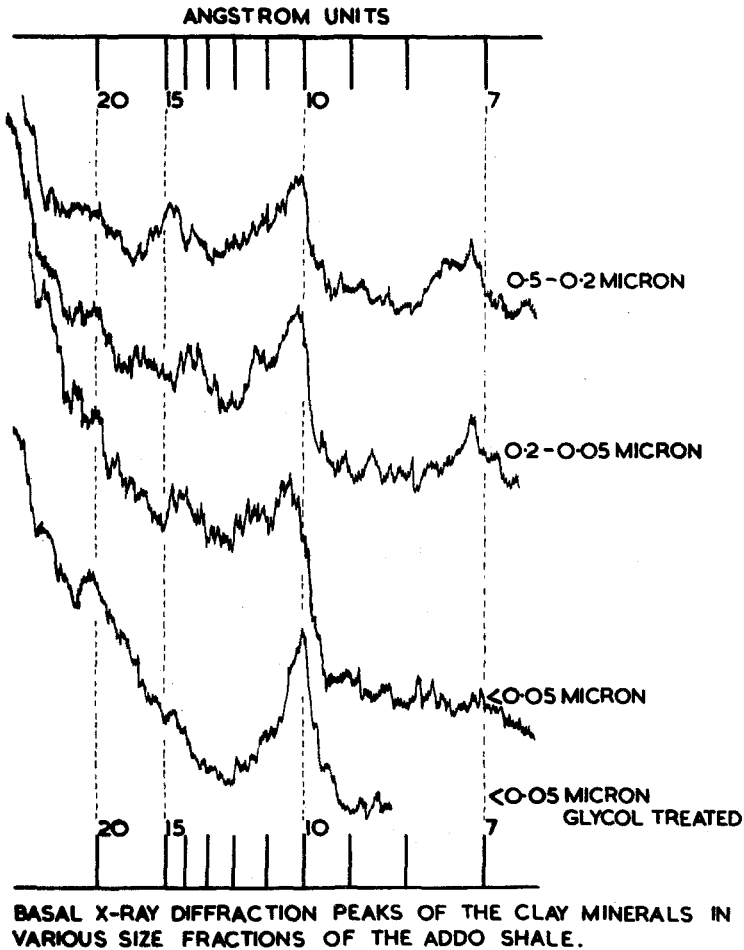


FIGURE 2

its consequences have been worked out by Brown and MacEwan (1950). These writers have shown that, when the difference between the two spacings is large, two peaks can appear. Thus, 10.0 Å and 15.4 Å layers present a single average reflection, while 10.0 Å and 17.7 Å layers (the latter corresponding to glycol-treated montmorillonite) give rise to a single, ill-defined peak when the proportions of montmorillonite layers are less than 20 percent and two observable peaks for higher proportions. One of these occurs at less than 10.0 Å, since it is a combination between the 10.0 Å spacing of illite and the second-order reflection from the 17.7 Å spacing. The other peak was not discussed by Brown and MacEwan (1950), but their calculated curves suggest that it occurs as a slight bump on the rapidly rising intensity curve observed at low angles, and corresponds to a spacing



higher than 17.7 Å. Similar curves calculated by the author confirm that this is the case. The appearance of the diffraction curve for the glycol-treated clay in Figure 2 is therefore in accord with expectation for a mixed-layer mineral.

The difference between 10.0 Å and the average 10.47 Å spacing observed for the clay in the natural state corresponds to about 15 percent of montmorillonoid layers (Brown and MacEwan, 1950). This seems hardly sufficient to give an observable separation of peaks in the glycol-treated clay. It has been repeatedly observed by the author, however, that, while 17.7 Å is the spacing obtained for glycol-treated Wyoming bentonite, the typical spacing for glycol-treated montmorillonites from South African soils is 18.8 Å. This appreciably larger spacing should make splitting distinctly easier, and this has been confirmed by carrying out calculations similar to those of Brown and MacEwan for a combination of 10.0 Å and 18.8 Å layers. Furthermore, as the second-order effect for 18.8 Å corresponds to 9.4 Å, combination with 10.0 Å should not give a spacing much below 10.0 Å when splitting takes place and this is also in accord with the results. The <0.05 micron fraction from the Addo shale was considered as representative of the "pure" mixed-layer mineral in these shales and was used to obtain the d.t.a., chemical analyses and X-ray data recorded in Figure 1, Table V, and Table VI, respectively.

TABLE V.—CHEMICAL ANALYSES OF CLAY MINERALS BELONGING TO THE HYDROUS MICA GROUP SEQUENCE

	Musco- vite <sup>1</sup>	Hydro- musco- vite Pre- toria <sup>2</sup>	Illite Gollel <sup>3</sup>	Random mixed- layer minerals		Regular mixed- layer mineral Burghers- dorp <sup>4</sup>	Mont- moril- lonite <sup>4</sup>
				Addo <sup>2</sup>	Alber- tina <sup>3</sup>		
SiO <sub>2</sub>	44.85	46.37	53.13	53.30	55.91	51.69	57.55
Al <sub>2</sub> O <sub>3</sub>	36.95	36.51	31.99	25.74	14.67	34.50	19.93
Fe <sub>2</sub> O <sub>3</sub>	1.54	0.96	1.18	3.76	10.36	0.19	6.35
FeO	1.36	—	—	—	—	—	0.95
TiO <sub>2</sub>	tr.	1.55	0.85	1.10	0.35	0.68	0.32
CaO	—	0.30	0.17	0.40	0.53	0.16	1.94
MgO	—	0.62	—	2.79	5.19	1.56	3.92
K <sub>2</sub> O	9.13	8.04	5.35	4.82	2.69	3.56	0.59
Na <sub>2</sub> O	1.78	1.16	0.18	0.33	0.25	1.03	0.33
Loss ign.	4.08	4.89	7.55	7.39	9.69	5.96	8.53
	99.69	100.40	100.40	99.63	99.64	99.33	100.41
Ion exchange capacity		2.5 m.e.	20.7 m.e.	34.7 m.e.	45.4 m.e.	48.0 m.e.	80 m.e.

<sup>1</sup> Jakob, J., *Zeits. Krist.*, 62, 443 (1925).

<sup>2</sup> Rethemeyer, R., National Chemical Research Laboratory, Pretoria.

<sup>3</sup> Sampson, D., National Chemical Research Laboratory, Pretoria.

<sup>4</sup> Grim, R. E., and Rowland, R. A., *Am. Mineral.*, 27, 746 (1942).

TABLE VI. — LATTICE SPACINGS IN ANGSTROM UNITS OF CLAY MINERALS BELONGING TO THE HYDROUS MICA GROUP SEQUENCE<sup>1</sup>

Hydromuscovite Pretoria	Illite Gollel		Random mixed-layer minerals				Regular mixed-layer minerals Burghersdorp		Montmorillonite (MacEwan)	
	d.	Int.	Addo		Albertinia		d.	Int.	d.	Int.
10.0	vs	vs	10.47	s	10.68	vs	25.8 <sup>2</sup>	vs	—	—
5.0	s	m	5.01	w	—	—	12.4 <sup>2</sup>	s	—	—
4.46	s	m	4.49	m	4.49	s	4.95	mw	—	—
4.28	w	w	4.25	w	4.26	w	4.47	s	4.60	vs
4.13	w	—	—	—	—	—	4.30	mw	—	—
3.86	m	—	—	—	—	—	—	—	—	—
3.72	m	w	3.71	w	—	—	3.67	w	—	—
3.48	m	—	—	—	—	—	—	—	—	—
3.34	vs	s	3.34	vs	3.34	m	3.33	m	—	—
3.19	mw	—	—	—	3.20	m	3.09	mw	—	—
2.987	ms	m	—	—	—	—	2.833	w	—	—
2.860	m	—	—	—	—	—	—	—	—	—
2.789	m	—	—	—	—	—	—	—	—	—
2.578	m	m	2.57	m	2.58	w	2.563	m	2.55	s
2.544	s	—	—	—	—	—	—	—	—	—
2.501	w	—	—	—	—	—	—	—	—	—
2.452	m	w	2.45	w	—	—	2.451	w	—	—

TABLE VI. — LATTICE SPACINGS IN ANGSTROM UNITS OF CLAY MINERALS BELONGING TO THE HYDROUS MICA GROUP SEQUENCE —  
Continued

Hydromuscovite Pretoria	Illite Gollel		Random mixed-layer minerals				Regular mixed-layer mineral Burghersdorp		Montmorillonite (MacEwan)		
	d.	Int.	Addo		Albertinia		d.	Int.	d.	Int.	
2.376	m	2.379	w	2.39	w	—	—	—	—	—	—
—	—	2.244	w	—	—	2.25	w	2.232	vw	2.217	vw
—	—	2.206	w	—	—	—	—	2.190	vw	—	—
2.143	m	—	—	—	—	—	—	2.145	vw	—	—
2.126	m	2.132	w	—	—	—	—	2.027	vw	—	—
1.997	m	2.011	m	—	—	—	—	1.997	vw	—	—
1.972	w	—	—	—	—	—	—	—	—	—	—
1.725	w	—	—	—	—	1.678	—	1.683	br	1.689	br
1.644	m	1.653	br	1.664	br	1.65	br	1.646	br	—	—
1.595	w	—	—	1.637	—	1.633	—	—	—	—	—
1.555	w	—	—	—	—	—	—	—	—	—	—
1.521	w	—	—	—	—	—	—	—	—	—	—
1.496	m	1.502	m	1.498	w	1.50	m	1.492	m	1.489	vs

<sup>1</sup> vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad.  
<sup>2</sup> After ethylene glycol treatment the values increase to 28.1 Å and 13.6 Å respectively.

On comparing the chemical analyses of the mixed-layer mineral from Addo with those of the hydromuscovite and illite and that of a typical montmorillonite (Table V), the intermediate position of the mixed-layer minerals becomes obvious. There is an increase in the  $\text{SiO}_2$ ,  $\text{MgO}$  and water content when progressing from the micas through the hydrous micas to the montmorillonoids, with a concomitant decrease in  $\text{Al}_2\text{O}_3$  and especially  $\text{K}_2\text{O}$ . The gradual increase of the cation exchange capacity in this sequence is also noteworthy.

The d.t.a. curve of the random mixed-layer mineral from Addo differs essentially from that of illite only in the higher intensity of the initial low temperature endothermal peak (Figure 1).

#### *Albertinia Clay*

In the Albertinia area the Bokkeveld shale is the parent rock of the silcretes, white clays and ochres (Haughton *et al.*), and also of the random mixed-layer clay mineral occurring on the farm Snymankraal, 9 miles north-west of Albertinia. The above mentioned deposits are considered to be Tertiary to Recent, and occur on a peneplain which is the chief physical characteristic of this area.

This green clay has an overburden of about 4 feet of soil. The clay becomes progressively lighter in color and from 8 feet down to 22 feet it is creamish to white. After removal of the overburden the clay is mined to a depth of about 5 feet and after being pulverised is marketed as a foundry clay. This material also lends itself to acid activation, after which it has excellent oil-bleaching and insecticide-adsorption properties.

The clay from Albertinia was also fractionated by sedimentation in water to remove the free silica and some kaolinite before the mixed-layer clay mineral was investigated in detail.

#### *Clay Mineralogy of the Albertinia Clay*

X-Ray diffraction analyses of samples collected at 1 foot intervals down to 22 feet below the surface indicated the presence of a hydrous mica, kaolinite and free quartz in the Albertinia clay deposit. The amount of kaolinite increased with depth as clearly shown by the X-ray diffraction diagrams (Fig. 3) of the untreated clay samples from various depths. The 7.2 Å basal diffraction peak, characteristic of kaolinite, progressively increases in intensity at 3-5 ft., 5-8 ft., 8-14 ft., and 14-18 ft. levels.

The appearance of the hydrous mica diffraction peaks is notably different for the clay samples collected at various depths. At 14-18 ft. the diffraction value of 10.0 Å indicates the presence of an illite, while at 8-14 ft. this mineral had obviously undergone some interlamellar hydration. The hydrous mica clay mineral at 5-8 ft. shows further development of the illite mineral into an illite-montmorillonite mixed-layer mineral, as indicated by the basal X-ray diffraction peak on the diagram reaching a maximum at about 10.4 Å and then gradually increasing in intensity in the direction of

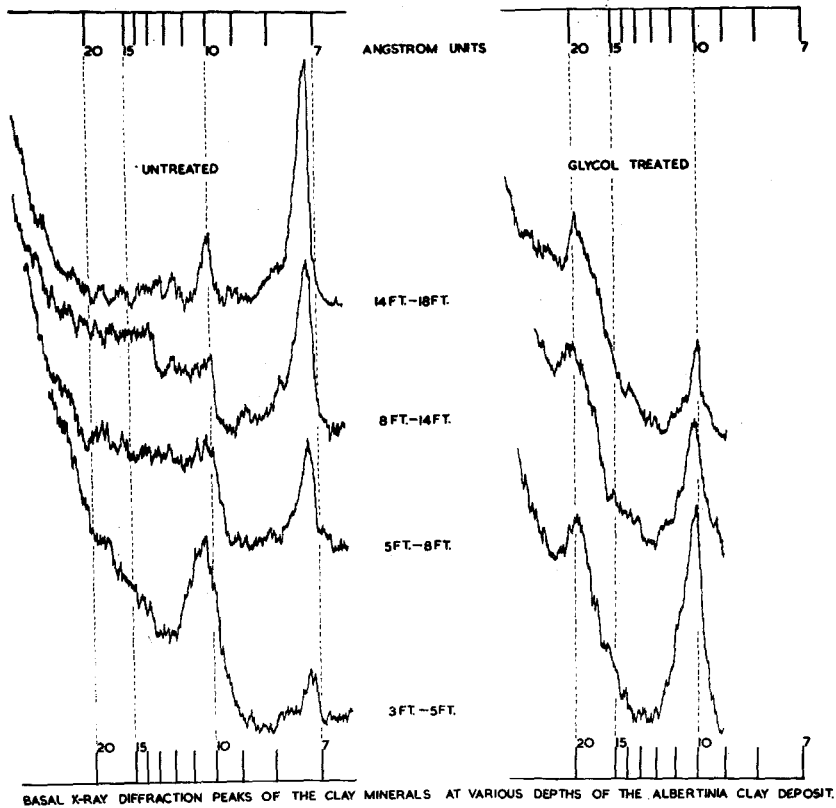


FIGURE 3

the primary X-ray beam. The clay sample at 3-5 ft. contained very little kaolinite and the hydrous mica is represented by a broad intense peak at 10.68 Å. When these samples, collected at various depths, were treated with ethylene glycol two basal X-ray diffraction peaks appeared at 10.0 Å and 20.0 Å in each case (Fig. 3). Following on the considerations already given for the Addo clay, these observations prove that the hydrous mica clay mineral in the Albertina clay is a random mixed-layer clay mineral. From the basal X-ray diffraction value of 10.68 Å the composition of the mixed-layer clay mineral is calculated to be 20 percent montmorillonite and 80 percent illite—a composition very similar to that of the Ordovician meta-bentonites (Weaver, 1953).

A comparison of the chemical analyses (Table VII) indicates that the increase of the ratio of kaolinite to mixed-layer clay mineral with depth is related to an increase in  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and a decrease in  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$  and loss on ignition. The increase in cation exchange capacity values also corresponds with an increase of the hydrous mica clay mineral.

TABLE VII.—CHEMICAL ANALYSIS OF ALBERTINIA CLAY AT VARIOUS DEPTHS<sup>1</sup>

	3 ft.-5 ft. Fractionated <sup>1</sup>	3 ft.-5 ft. Unfrac- tionated <sup>1</sup>	5 ft.-9 ft. <sup>1</sup>	8 ft.-14 ft. <sup>1</sup>
SiO <sub>2</sub>	55.91	58.25	62.43	64.45
Al <sub>2</sub> O <sub>3</sub>	14.67	15.76	16.19	17.30
Fe <sub>2</sub> O <sub>3</sub>	10.36	6.72	7.29	5.73
TiO <sub>2</sub>	0.35	0.65	1.14	0.71
CaO	0.53	0.95	0.79	0.34
MgO	5.19	4.08	1.54	1.74
K <sub>2</sub> O	2.69	2.48	2.49	1.54
Na <sub>2</sub> O	0.25	0.80	0.70	1.03
SO <sub>3</sub>	0.50	—	—	—
Ign. loss	9.69	8.67	7.19	7.43
	100.14	99.36	99.76	100.27
Ion exchange capacity	45.4 m.e.	34.7 m.e.	30.3 m.e.	27.0 m.e.

<sup>1</sup> Sampson, D., National Chemical Research Laboratory, Pretoria.

A fractionated sample of the material occurring at 3-5 ft. was treated to remove all the free quartz and kaolinite, and a chemical analysis, a d.t.a. curve and X-ray data of this "pure" random mixed-layer clay mineral are given in Table V, Figure 1, and Table VI, respectively. As in the case of the random mixed-layer clay mineral occurring in the Addo shale, the hydrous mica clay mineral in the Albertinia clay has properties intermediate between those of the typical illites and the montmorillonoids.

It appears logical that the Bokkeveld shales were the parent rock of the Albertinia random mixed-layer clay mineral when it is considered that the predominant clay mineral in the Bokkeveld shale occurring near Addo station is also a random mixed-layer clay mineral with only slightly less montmorillonoid inter-layers (*i.e.* 15 percent compared to 20 percent in the Albertinia clay). A comparison of chemical analyses of the Bokkeveld shale and the above mentioned mixed-layer clay minerals supports this view on the derivation of the Albertinia clay (Table VIII).

The analysis of the main adsorbed cations of the random mixed-layer clay mineral from Albertinia, namely:

CaO	9.2 m.e.
MgO	12.9 m.e.
and Na <sub>2</sub> O	15.9 m.e.

would indicate the deposition of the clay in a marine or estuarine environment.

#### D. A REGULAR MIXED-LAYER MINERAL

In the random mixed-layer minerals no spacings larger than the average basal spacing are to be expected. If, however, the arrangement is regular,

TABLE VIII. — CHEMICAL ANALYSES OF:

	Bokkeveld shales near Riversdale <sup>1</sup>		Mixed-layer mineral Addo <sup>2</sup>	Mixed-layer mineral Albertinia <sup>3</sup>
SiO <sub>2</sub>	68.78	67.58	53.30	55.91
Al <sub>2</sub> O <sub>3</sub>	14.98	15.62	25.74	14.67
Fe <sub>2</sub> O <sub>3</sub>	4.94	5.86	3.76	10.36
TiO <sub>2</sub>	—	—	1.10	0.35
CaO	0.50	0.48	0.40	0.53
MgO	1.87	2.43	2.79	5.19
K <sub>2</sub> O	2.42	2.01	4.82	2.69
Na <sub>2</sub> O	2.04	1.95	0.33	0.25
SO <sub>3</sub>	—	—	—	0.50
Loss ign.	3.33	3.58	7.39	9.69
	99.86	99.51	99.63	100.14

<sup>1</sup> Visser, D. J. L., *Bull. Geol. Surv. S. Afr.*, No. 9, p. 10 (1937).

<sup>2</sup> Rethemeyer, R., National Chemical Research Laboratory, Pretoria.

<sup>3</sup> Sampson, D., National Chemical Research Laboratory, Pretoria.

the diffraction effect is equivalent to a larger unit cell which is a multiple of the individual layers.

A regular mixed-layer clay mineral (1:1 illite and montmorillonite layers) occurs about twelve miles south-east of Burghersdorp in the Cape Province. In the natural material 12.4 Å and 25.8 Å peaks are noticed that moved to 13.6 Å and 28.1 Å respectively after glycol treatment. If the 25.8 Å reflection is regarded as 10 Å + 15.8 Å, the shift to 28.1 Å, *i.e.*, 10 Å + 18.1 Å on glycol treatment is in accord with expectations.

This clay is being used in the ceramic industry as a component of an insulator body, in which it acts as a bond in the green ware and as a flux on firing. The finely ground clay is white enough to be used successfully as a filler for high grade paper.

The clay is associated with intrusions of dolerite sheets into the Molteno shales, resulting in hydrothermal alteration of the illite in the latter to a mixed-layer clay mineral.

This clay occurrence has been discussed in detail elsewhere (Heystek, 1954), and is only mentioned in this paper to demonstrate its intermediate chemical and X-ray characteristics when compared to the other hydrous micas (Tables V and VI).

#### E. CONCLUSIONS ON HYDROUS MICAS IN SOME CLAYS AND SHALES

On summarising the results obtained from the investigation of A. The hydromuscovite from Pretoria, Transvaal; B. The illite from Gollel, Swaziland; C. The random mixed-layer clay mineral from Addo, Cape Province (15 percent montmorillonite, 85 percent illite), and the random

mixed-layer clay mineral from Albertinia, Cape Province (20 percent montmorillonite, 80 percent illite) and D. The regular mixed-layer clay mineral from Burghersdorp, Cape Province (50 percent illite, 50 percent montmorillonite) the following observations can be made:

(i) The basic crystalline structure of the minerals, micas — hydromuscovites — illites — mixed-layer minerals — montmorillonites, is very similar. A gradual decrease in crystallinity indicated by some reflections becoming weaker or disappearing may also be noticed by comparing the X-ray diagrams (Fig. 4) and/or d-values (Table VI) of the well-crystallised micas with those of the hydrous micas (intermediate properties) and the poorly crystalline montmorillonoids respectively.

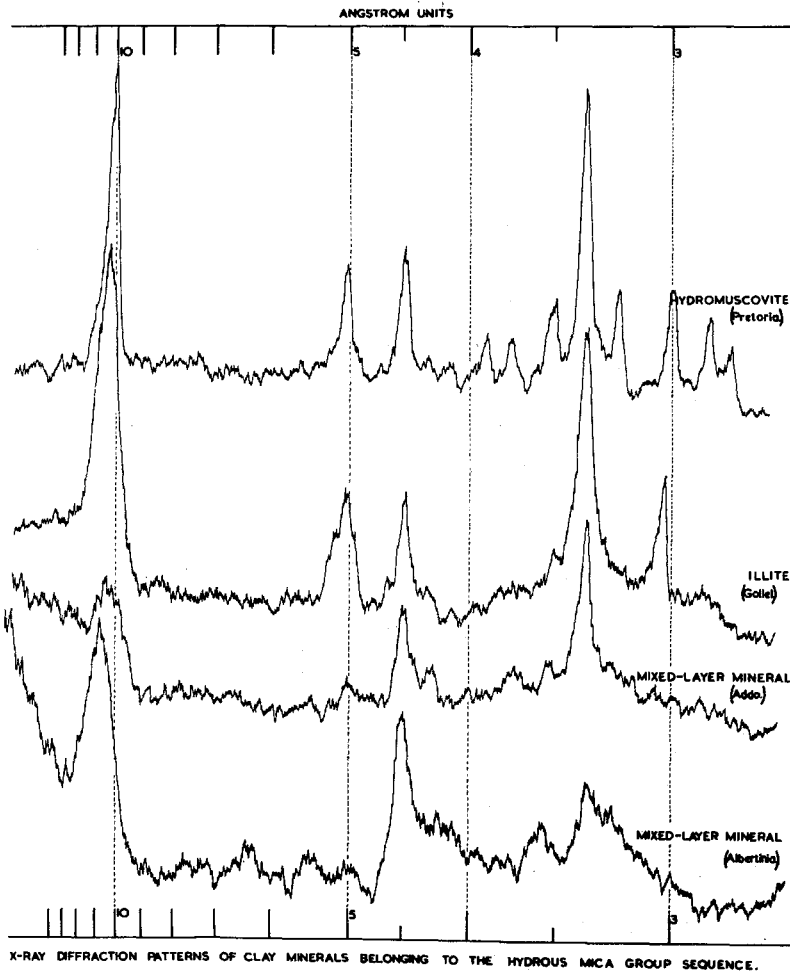


FIGURE 4



(ii) Although the hydromuscovite and illite clay minerals give a characteristic d.t.a. curve (Fig. 1) it is obvious that d.t.a. methods alone cannot positively identify the presence of mixed-layer clay minerals. There is no marked difference between the d.t.a. curves of the mixed-layer clay minerals and the type of curve obtained for numerous montmorillonoids.

(iii) A comparison of the chemical analyses of the hydrous mica clay minerals (Table V) shows that on passing through the sequence micas — hydrous micas — montmorillonites, a decrease in  $K_2O$  content is the most marked change.

The crystalline structure of the illite from Gollel is similar to that of the hydromuscovite except that about 15 percent of the  $Si^{++++}$  positions are occupied by  $Al^{+++}$  (refer to calculated formulas). In the hydromuscovite about 25 percent of the  $Si^{++++}$  positions are occupied by  $Al^{+++}$ , and the resulting excess charges are satisfied by a proportionately greater number of  $K^+$  ions between the silica sheets of two successive units. The  $K^+$  ions act as bridges joining the units together so that they do not expand in the presence of water.

The montmorillonite structure is similar to that of illite except that most of the lattice substitution positions occur in the octahedral layer and consequently the units are loosely held together in the direction of the c-axis with water and exchangeable ions present between them. As a result, when the proportion of montmorillonite layers increases in relation to the illitic layers in the mixed-layer minerals as represented by the clay minerals from Addo and Albertinia respectively, the amount of fixed  $K^+$  decreases gradually. At the same time the water content and ion exchange capacity increases.

The clay minerals discussed in this paper (dioctahedral in all cases) can be placed as follows in the generally accepted tentative classification for hydrous micas:

#### HYDROUS MICAS

- I. *Hydromuscovites*  
(from Pretoria)
- II. *Illites*  
(from Gollel)
- III. *Mixed-layer structures*
  - (i) Regular (Burghersdorp)
  - (ii) Random (Addo)  
(Albertinia)

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