An occurrence of a regular mixed-layer clay-mineral.

By H. Heystek.

National Chemical Research Laboratory, South African Council for Scientific and Industrial Research, Pretoria.

[Communicated by the General Secretary; taken as read March 25, 1954.]

I. Introduction.

ABOUT twelve miles south-east of Burghersdorp in the Cape Province, South Africa, the unusual clay reported in this paper was first discovered on the farms 'Groenvlei' and 'Kuilfontein'. Later deposits were also uncovered on the farms 'Kapokkraal' and 'Kleinhoek'.

The clay-mineral appears to be of a very unusual type, namely, a regular mixed-layer clay-mineral (1:1 hydrous mica and montmorillonite). The mode of origin of the clay is also of interest in that it appears to be produced from a shale by hydrothermal alteration, due to intrusion of dolerite sheets.

The clay, owing to absence of iron, appears white in colour and burns white. It is thus being used in the ceramic industry as a member of an insulator body, where it acts as a bond in the green ware and as a flux upon firing of the product. Finely ground, the clay can also be used successfully as a filler for high-grade paper.

II. Occurrence.

Geologically, the area in which the clay occurs comprises the Upper Beaufort and the sandstones and shales of the Molteno beds with numerous intrusions of dolerite sheets. In all the known occurrences the clay appears at a contact zone between a thick dolerite sheet and the Molteno shales.

The white clay is usually found at or near the contact with a dolerite sheet. It is a compact material, with a hardness of 2, a smooth feel, and a conchoidal fracture. Black dendritic growths appear on some fracture surfaces. The thickness of this white material varies between 2 and 5 feet and then progresses into material with a cream or yellow colour. On moving farther away from the dolerite sheet the typical Molteno shales, yellow or grey in colour, are found.

Geologically, the appearance of the clay seems to be associated with an intrusion of dolerite into the Molteno shale, and its probable genesis is a hydrothermal alteration of these shales. The hydrothermal alteration was presumably not very intense, but merely resulted in the progressive hydration of the illitic clay minerals of the Molteno shale, with accompanying removal of silica and iron. Without doubt more deposits will be uncovered in the future within the vicinity of the known occurrences which are extensive and already worked economically.

III. Chemical analysis.

In table I the chemical analyses are given of the white clays on the farms 'Kuilfontein' and 'Groenvlei' and also tabulated are analyses of the yellow clay and of Molteno shale from the deposit on the latter farm. Depths below the intrusion are indicated.

Table I. Chemical analyses of Burghersdorp clays.

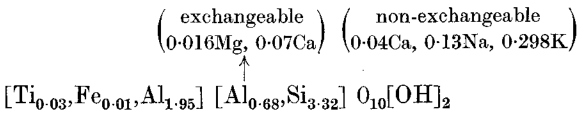
	White clay.		Yellow clay.	Molteno shale.	
	Kuil-fontein.	Groenvlei.	Groenvlei.	Groenvlei.	
	1 foot.	1 foot.	5 feet.	9 feet.	15 feet.
SiO_2	52·02	51·69	59·44	63·06	72·51
Al_2O_3	34·18	34·50	28·47	26·26	18·79
Fe_2O_3	0·58	0·19	1·36	1·22	0·59
TiO_2	0·68	0·68	0·76	0·70	0·84
MgO	0·41	0·16	0·17	—	0·10
CaO	1·44	1·56	1·15	0·94	0·71
Na_2O	1·02	1·03	1·15	0·49	0·17
K_2O	3·19	3·56	2·34	2·32	2·90
SO_3	0·23	0·12	0·06	0·27	0·03
ign. loss	6·79	5·96	5·47	5·50	3·66
	100·54	99·45	100·37	100·76	100·30
Base-exchange capacity	45 m.e.	48 m.e.	41·5 m.e.	24·8 m.e.	10·5 m.e.

(Analyses by D. Sampson on dry basis 110° C.)

The yellow clay differs essentially from the white clay in that its iron content is higher and that it contains free quartz (as proved by X-ray diffraction data). The underlying Molteno shale also shows a progressive increase in quartz content. It is clear that no sharp boundaries exist and that the Molteno shale at 9 feet is considerably altered. The sample at 15 feet may be regarded as unaltered shale.

As will be shown later, the only minerals which could be detected in the unaltered shale were quartz and illite. The relative proportions could not be measured, but, if it is assumed that free quartz forms about 45 % of the shale, the remainder of the analysis conforms reasonably well to that of an illite. If the various depths can be regarded as stages in the process of alteration, we can say that the main change, apart from the alteration of the clay-mineral, is removal of the large amount of free quartz. Iron is also removed in the white clay nearest the intrusion, but appears to accumulate at farther distances. Part of the potassium is also lost, since removal of free quartz would otherwise lead to the presence of 5–6 % K_2O in the altered material.

From the analysis of the white clay from 'Groenvlei' the following formula can be calculated:



$$\begin{array}{c} \begin{pmatrix}\text{exchangeable}\\ 0{\cdot}016\text{Mg},\ 0{\cdot}07\text{Ca}\end{pmatrix} \begin{pmatrix}\text{non-exchangeable}\\ 0{\cdot}04\text{Ca},\ 0{\cdot}13\text{Na},\ 0{\cdot}298\text{K}\end{pmatrix} \\ \uparrow \\ [\text{Ti}_{0\cdot03},\text{Fe}_{0\cdot01},\text{Al}_{1\cdot95}]\ [\text{Al}_{0\cdot68},\text{Si}_{3\cdot32}]\ \text{O}_{10}[\text{OH}]_2 \end{array}$$

On the evidence to follow, the mineral has a mixed-layer structure, so that, if differences in chemical composition occur between the two types of layers, the above formula must be regarded as an average. The Mg^{++}, Ca^{++}, Na^{+}, and K^{+} are interlayer cations. Using the ammonium-acetate Kjeldahl distillation method of base-exchange determination, a base-exchange value of 48 m.e. per 100 g. clay dried at 110° C. was found. The ammonium-acetate leach liquor was also analysed and found to contain Mg^{++} and Ca^{++} in proportions corresponding to 46 m.e. per 100 g. clay, confirming the value from Kjeldahl distillation. This corresponds to all the Mg^{++} and about two-thirds of the Ca^{++} of the natural occurring clay. Analysis of the ammonium-acetate treated clay confirmed that this amount of Mg^{++} and Ca^{++} had been removed.

One-third of the Ca^{++} and all of the Na^{+} and K^{+} were found to be non-exchangeable by NH_4^{+} or any other cation. The 3·56 % of fixed potassium oxide is characteristic of illite, although distinctly smaller in percentage than in true illites. Non-exchangeable Na^{+} and Ca^{++} are presumably trapped between non-expanding layers along with the K^{+}.

The base-exchange capacity appears too high for an illite and too low for a montmorillonite, suggesting that the clay is in some way a mixture of the two. Many clays consist of mixtures (1) in such a way that discrete particles of the individual minerals occur, with no preferred geometric orientation of one clay particle with respect to its neighbours. Another type of mixing, however, first reported by Gruner (2), is the interstratification of parallel layers of separate minerals. In recent years such 'mixed-layer minerals' have frequently been reported (3, 4, 5), and it appears to represent a common mode of formation of clay minerals in deposits of hydrothermal origin (6, p. 325). Many earlier clay-mineral species such as beidellite (7), bravaisite (4), &c., are now recognized as mixed-layer minerals.

Mixed-layer minerals are of two types: (i) those in which the succession of the two types of layers is random; and (ii) those in which two types of layers are arranged in a regular order. The distinction between these must be made on the grounds of X-ray diffraction data.

IV. X-RAY DIFFRACTION DATA.

X-ray powder diffraction patterns were obtained with a Philips high-angle spectrometer goniometer, type 42201/2, with Co-$K\alpha$ radiation (λ 1·78890) and an automatically recording Brown Electronik strip-chart potentiometer.

From a total of 49 X-ray diffraction diagrams it was possible to determine the X-ray diffraction data for the pure clay-mineral (although a mixture in itself) as it occurs in the natural state (table II). The white clay usually contained no other admixed minerals except free quartz in the deposits on 'Kapokkraal'. In all the deposits, the underlying yellow-coloured clay and the Molteno shales respectively showed increasing amounts of free quartz.

TABLE II. X-ray data for Burgersdorp clay.

d.	Int.	*d.*	Int.	*d.*	Int.	*d.*	Int.
25·8*	vs	3·67	w	2·451	w	1·977	vw
12·4*	s	3·33	m	2·232	vw	1·683	w b
4·95	mw	3·09	mw	2·190	vw	1·646	
4·47	s	2·833	w	2·145	vw	1·492	m
4·30	mw	2·563	m	2·027	vw	1·287	w

* On ethylene glycol treatment the values increase to 28·1 and 13·6 Å. respectively.

The samples from the 'Groenvlei' occurrence, chemical analyses of which are given in table I, were used for comparison. Apart from peaks in the region of the basal spacing, all showed a diffraction pattern, which, except for the occurrence of quartz, corresponded completely to a dioctahedral illite or hydrous mica (8). The peaks representing the basal spacing and higher spacings are reproduced in fig. 1. The unaltered shale at 15 feet shows a well-defined peak at 9·99 Å., and the clay mineral present must therefore be regarded as illite. In the sample at 9 feet, this peak is distinctly weaker and shows a broadening towards higher spacings. In the yellow clay, this process has advanced farther with the highest intensity of the broad peak at 12·4 Å. and the appearance of a new peak at a spacing of 25·8 Å. The white clay shows intense, sharp peaks at 12·4 Å. and 25·8 Å. only. This indicates that the main alteration in the clay-mineral according to the X-ray investigation is a progressive hydration, resulting in an increase of the basal spacing.

Drying the clay at 145° C. and 500° C. showed a progressive movement of the 12·4 Å. X-ray diffraction peak to 10·47 Å. and 9·94 Å. respectively, while the 25·8 Å. peak decreased in intensity and ultimately disappeared. The clay then slowly rehydrated to its original state when left at room conditions again. Ethylene glycol treatment caused an increase of the 12·4 Å. and 25·8 Å. values to 13·6 Å. and 28·1 Å. respectively. These properties again indicated the presence of a clay-mineral with an expandable lattice, i.e., of montmorillonite (fig. 2).

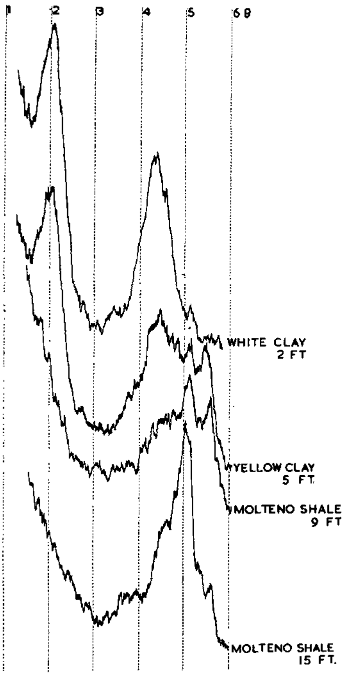


Fig. 1.

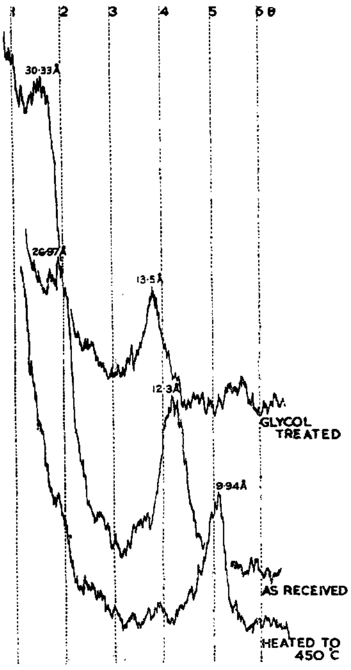


Fig. 2.

Basal X-ray diffraction peaks of:

Fig. 1. The clay profile, showing progressive alteration of illite to a mixed-layer clay-mineral.

Fig. 2. Mixed-layer clay-mineral after various treatments.

It would thus appear that X-ray data, in agreement with the chemical analysis and base-exchange properties, indicate the presence of both an illitic or hydrous mica mineral and of a montmorillonitic mineral.

Attempts to obtain only a montmorillonite or illite typical basal X-ray diffraction peak value by $MgCl_2$ (9), $CaCl_2$ (4), or KOH (10) treatments of the original white clay failed.

If the two clay-minerals were present as a mixture, the basal reflection at 12·4 Å. should not appear. Instead, separate reflections at 10 Å. and 15·4 Å. should occur in the natural clay, and at 10 Å. and 17·7 Å. in the glycol-treated clay. It seems clear therefore that the present mineral is a mixed-layer type.

The mathematical theory of X-ray diffraction for random mixed-layer structures has been presented by Hendricks and Teller (11), and further developed by Brown and MacEwan (8). In a random structure, an average basal spacing is to be expected, such as the 12·4 Å. and the 13·6 Å. (glycol-treated) in the present case. These spacings suggest that montmorillonite and hydrous mica layers are present in roughly a 1:1 ratio, and this is also in accord with the base-exchange capacity.

In a random stratification, no spacings larger than the average basal spacing are to be expected. If, however, the arrangement is regular, the diffraction effect is equivalent to a larger unit cell which is a multiple of the individual layers. In the present case, a distinct reflection at 25·8 Å. in the natural occurring white clay must be taken as proof of a regular structure, based on a 1:1 ratio. If this is regarded as 10–15·8 Å., the shift to 28·1 Å., i.e., 10–18·1 Å. on glycol treatment is in accord with expectations. So also is the disappearance of these reflections on heating, since a montmorillonite layer on dehydration presents a basal spacing at 10 Å. which does not differ significantly from that of an illite layer. The only previous record of a clay mineral with regular alternating layers is that of rectorite by Bradley (12), with a first-order spacing of 25 Å., shifting to 26·6 Å. with ethylene glycol. This was interpreted as a 1:1 ratio of pyrophyllite to vermiculite.

With a 1:1 ratio, the second-order reflection for the higher spacing falls in the same position as the average of the individual basal spacings and cannot therefore be distinguished from it. No evidence for a third-order reflection at 8·6 Å. was obtained with any sample.

If the regularity of the 1:1 arrangement were perfect the mean basal spacing should be exactly equal to half of the higher spacing, i.e., in this case it should be 12·9 Å. instead of 12·4 Å. The difference can only be accounted for if we postulate that the ratio of hydrous mica: montmorillonite is a little in excess of 1:1. The additional hydrous mica layers would be inserted at random in the structure, and would give rise to a decrease of the mean basal spacing. Such insertions of course impair the regularity of the 1:1 arrangement, thereby tending to make the peak due to the higher spacing less sharp and less intense. Only a moderate excess of hydrous mica layers distributed in this way would suppress the higher spacing reflection altogether.

It is of interest to note that the greatest regularity was not found where alteration was most intense. The sample of white clay in fig. 1 was taken about 2 feet away from the intrusion, while a sample of white clay taken next to the intrusion is illustrated in fig. 2. It will be seen that for much the same second-order basal spacing, the higher spacing is distinctly larger but gives a much less well-defined peak. On glycol treatment it also shows a greater shift. It is not proposed to discuss the significance of these differences in detail, but it is clear that they correspond to a less regular structure.

When the Ca^{++}, Mg^{++}, H^{+}, NH_4^{+}, K^{+}, Na^{+}, Li^{+}, and Ba^{++} clays were prepared by treating the clay with either the acetate or chloride salts of these cations the basal reflections shifted to the extent of the amount of layers of water adsorbed (13) by the montmorillonite member of the mixed-layer mineral. The various exchangeable cations gave the following results: Ca^{++} 12·27, Mg^{++} 11·99, and H^{+} 12·51 Å., showing two molecular layers of water adsorbed by the expandable layer; while NH_4^{+} 10·8, K^{+} 10·8, Na^{+} 10·8, Li^{+} 11·0, and Ba^{++} 11·0 Å., indicated the presence of a monomolecular layer of water within the expandable layer.

V. Differential thermal analysis.

The automatic differential thermal analysis apparatus used in this laboratory has been described fully by Theron (14) and the differential thermal holder by the author (15) in an earlier publication. All the differential thermal curves were obtained by heating material dried at 80° C. at a rate of 15° C. per minute and using the same sensitivity scale (220 μv.) on the recording meter. From 38 differential thermal runs representative curves are reproduced in fig. 3, again of the profile at the deposit on 'Groenvlei'.

The Molteno shale at 15 feet gives a typical curve for illite, while the Molteno shale at 9 feet shows already some signs of alteration, namely, more intense endothermal peaks, and a slight change in shape of the second endothermal peak. The fully developed alteration is shown by the white clay with a curve that compares well with reported mixed-layer differential thermal curves in the literature (6, 8). The yellow clay gave the same curve as the white clay and is not reproduced. The main differences between the curve for illite and that for the mixed-layer mineral is a general intensification of the reactions and the appearance of a new endothermic reaction at 700° C. in the latter mineral.

As in the case with the X-ray investigation, the differential thermal analysis results substantiate the theory of the alteration of the shale into the mixed-layer clay-mineral due to hydrothermal changes following the dolerite intrusions.

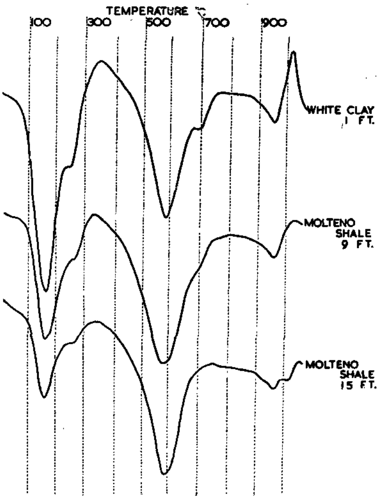


Fig. 3. Differential thermal curves of the clay profile, showing progressive alteration of illite to a mixed-layer clay-mineral.

Discussion of mode of alteration.

From the facts in the previous sections it becomes possible to form some picture of the mode of alteration of the original illite to a mixed-layer mineral. It seems reasonable to postulate that this takes place by hydration of alternate layers, accompanied by the removal of potassium from such layers. In the shale at 9 feet the chemical analysis (table I) indicates that the change has probably taken place to a marked extent. This is not necessarily in agreement with the X-ray diffraction data (fig. 1), since replacement of the 10 Å. peak by a 12·4 Å. peak and the appearance of a higher spacing are only to be expected when the alteration is nearly complete, i.e., when the hydrous mica:montmorillonite ratio approaches unity throughout the whole of the clay-mineral. In the yellow clay, despite the marked changes in the basal X-ray diffraction pattern, there is probably not much further alteration of the clay-mineral. The most complete change is evidenced by the white clay, but even in this case, as already discussed, there is evidence that the structure is not completely regular. This is to be expected from the mode of formation, since this is bound to lead to faults in the regularity, i.e., occasionally two hydrous mica layers will be sandwiched between montmorillonite layers instead of a single layer.

It can well be understood that conditions next to the intrusion are too intense for alteration to take place in a completely regular manner, and this would explain the type of X-ray diagram shown in fig. 2.

According to the above view-point, every second layer of the original illite should remain undisturbed. In such a case, since sodium is non-exchangeable, the sodium to potassium ratio should not alter. The analyses in table I, however, indicate that there is a higher ratio of sodium to potassium after alteration has taken place. If the sodium content of 0·17 % is truly representative of the unaltered shale, it has to be admitted that this seems contrary to the theory suggested above.

Acknowledgements.—Thanks are due to Dr. P. C. Carman for his constructive criticism. This paper is published with the permission of the South African Council for Scientific and Industrial Research.

References.

1. Grim (R. E.), Modern concepts of clay minerals. Journ. Geol. Chicago, 1942, vol. 50, pp. 225–275. [M.A. **8**–294.]
2. Gruner (J. W.), The structure of vermiculites and their collapse by dehydration. Amer. Min., 1934, vol. 19, pp. 557–575. [M.A. **6**–181.]
3. Hendricks (S. B.) and Jefferson (M. E.), Crystal structure of . . . mixed vermiculite-chlorites. Amer. Min., 1938, vol. 23, pp. 851–862. [M.A. **7**–397.]
4. Nagelschmidt (G.), X-ray diffraction experiments on illite and bravaisite. Min. Mag., 1944, vol. 27, pp. 59–61.
5. MacEwan (D. M. C.), Some notes on the recording and interpretation of X-ray diagrams of soil clays. Journ. Soil Science, 1949, vol. 1, pp. 90–103.
6. Grim (R. E.), Clay mineralogy. New York, 1953. [M.A. **12**–184.]
7. —— and Rowland (R. A.), Differential thermal analysis of clay minerals . . . Amer. Min., 1942, vol. 27, pp. 746–761. [M.A. **9**–76.]
8. Brindley (G. W.), editor, X-ray identification and crystal structures of clay minerals, 1951. Mineralogical Society, London.
9. White (J. L.), Transformation of illite into montmorillonite. Proc. Soil Sci. Soc. Amer., 1951, vol. 15 (for 1950), pp. 129–133. [M.A. **11**–546.]
10. Weaver (C. E.), Mineralogy and petrology of some Ordovician K-bentonites and related limestones. Bull. Geol. Soc. Amer., 1953, vol. 64, pp. 921–943.
11. Hendricks (S. B.) and Teller (E.), X-ray interference in partially ordered lattices. Journ. Chem. Phys., 1942, vol. 10, pp. 147–167.
12. Bradley (W. F.), The alternating layer sequence of rectorite. Amer. Min., 1950, vol. 35, pp. 590–595. [M.A. **11**–454.]
13. Barshad (I.), The effect of the interlayer cations on the expansion of the mica type crystal lattice. Amer. Min., 1950, vol. 35, pp. 225–238. [M.A. **11**–221.]
14. Theron (J. J.), An improved apparatus for the differential thermal analysis of minerals. Brit. Journ. Applied Phys., 1952, vol. 3, pp. 216–220.
15. Heystek (H.) and Chase (B. M. R.), A study of the brown plastic clays occurring in the Transvaal. Trans. Brit. Ceram. Soc., 1953, vol. 38, pp. 482–496.