A REGULARLY INTERSTRATIFIED MONTMORILLONITE-CHLORITE

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ABSTRACT

A mixed layer clay mineral having a regular alternation of montmorillonite- and chlorite-like layers is described using x-ray, thermal, dehydration, and chemical analysis. X-ray examination of the natural material shows a long spacing of about 29 Å and a fairly well developed sequence of basal spacings. The montmorillonite-like layers expand with glycerol and contract with heat treatment similar to montmorillonite while the chlorite-like layers show modified reflection intensities on heating similar to chlorite. The electron distribution normal to (001) indicates the presence of regular interstratification. Dehydration and thermal analyses yield curves which can be accounted for by attributing water loss reactions to montmorillonitic and chloritic material. The high MgO content of the clay lends support to the presence of chloritic layers. The question of nomenclature of such materials is raised.

INTRODUCTION

The dominant clay mineral occurring in the Yates Formation, Ward County, Texas, is a mixed-layer variety having a highly regular alternation of montmorillonite- and chlorite-like layers. Core samples containing this mineral were made available for study by the Fort Worth Production Division of the Gulf Oil Corporation.

The occurrence of *randomly* stratified layer silicates is a general phenomenon found as a transition stage in the alteration of non-expanding layer silicate minerals such as micas and chlorites, to the expanding minerals montmorillonite and vermiculite, but only a few instances are known of regular interstratifications. Examples have been described by Bradley (1950)(1), Sudo et al. (1954)(2), Heystek (1954)(3), and Lippmann (1954)(4). A preliminary x-ray examination of the clay mineral in the Yates Formation indicated that this material might be suitable for detailed study.

OCCURRENCE

Geologically, the clay occurs somewhat irregularly distributed in argillaceous siltstone from the Upper and Lower Yates Formation of Permian age in West Texas. The siltstone is poorly cemented and varies in color from light gray to gray-brown with numerous blue-gray streaks. Thin sections of the cores revealed quartz, clay and carbonaceous matter, feldspar, dolomite, and mica in order of abundance. The clay minerals

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occur dispersed throughout the rock and as cementing material, although the montmorillonite-chlorite is more abundant in the dark areas. The small platy black particles of carbonaceous matter are concentrated in, although not limited to, the blue gray streaks. Clay fractions of the siltstone containing primarily montmorillonite-chlorite were used for the study.

X-Ray Analysis

X-ray diffractometer records of the $<1\mu$ clay fraction in the natural and glycerol-solvated states show well-defined reflections from spacings

TABLE 1. MONTMORILLONITE-CHLORITE: X-RAY POWDER DATA
$<0.2\mu$ FRACTION, (FILTERED CuKα RADIATION, λ 1.5418 Å)

I (Est.)	dÅ (Meas.)	I (Est.)	dÅ (Meas.)
8 p	14.1	7 m	2.58
2 m, p	10.02	4 b	2.43
8 p	9.07	2 b, m	2.32
5 p	6.94		2.21
5 p	5.51	3 b, m	1.99
4 m, p	5.05	2	1.74
10	4.62	4	1.70
3 m	4.51	1 m	1.67
4	3.85	8	1.54
10 p	3.45	4 m	1.50
3 m	3.05	2	1.32
2	2.87	2 m	1.30
2	2.76		

b = broad lines.
m = mica lines.
p = preferred orientation.

of about 29 Å and 32 Å, respectively (see Fig. 1), which are assumed to be first order basal reflections. Although the diffractometer is well suited for the study of basal reflections, the powder photographic method has advantages in revealing the full diffraction pattern which is given in Table 1. However, the presence of minerals such as mica in the $<1\mu$ fraction has precluded presentation of reliably indexed powder diffraction lines. A strong reflection at 1.542 Å and a medium strong reflection at 1.505 Å are recognized as the (060) reflections from the montmorillonite-chlorite and mica, respectively. These values lie in the ranges associated with trioctahedral and dioctahedral layer silicates. Corresponding (020) reflections are observed also, and their diffuseness points to the presence of layer displacements which are common in clay mineral structures.
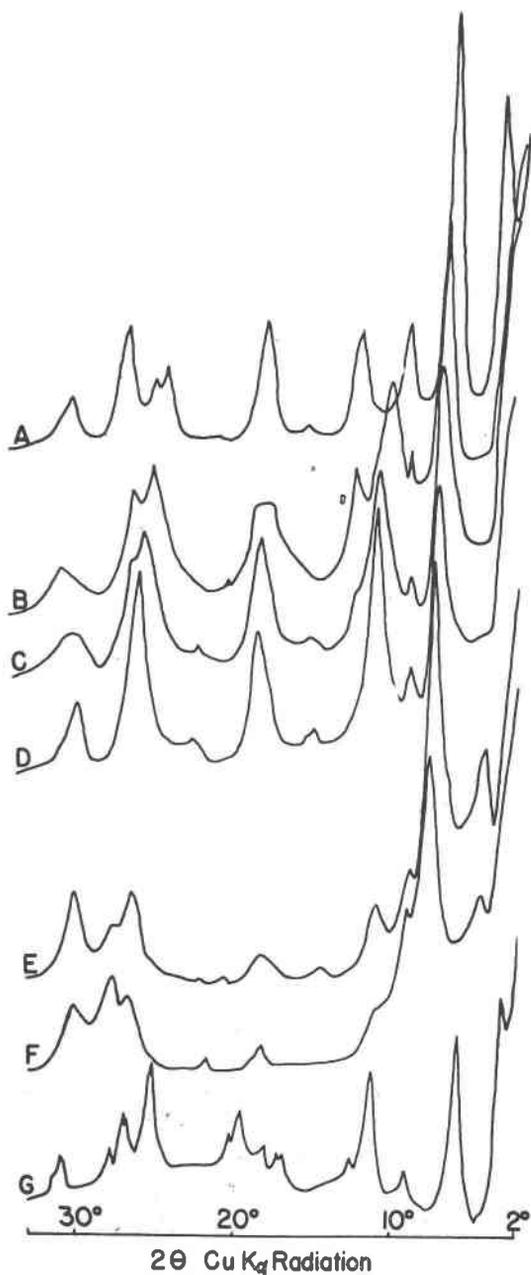
FIG. 1: X-Ray diffractometer patterns of montmorillonite-chlorite from argillaceous siltstone, Ward County, Texas, prepared from <.5μ fraction by sedimentation on glass slides to yield maximum preferred orientation. A—Unheated, room air; B—85° C., dry air; C—200° C., dry air; D—400° C., room air; E—550° C., room air; F—700° C., room air; G—glycerol saturated, room air.

On the supposition that montmorillonite-chlorite might have hexagonal symmetry, an attempt was made to index the pattern using Bunn charts. Lack of success limited the determination of the unit cell to the b parameter:

$$b = 6 \times 1.542 = 9.25 \text{ Å}$$

This value is comparable with the b parameters of chlorites which lie in the range 9.20 to 9.35 Å, the lower value corresponding to Mg-rich chlorite and the higher value to Fe-rich chlorite. The b parameter for Mg-montmorillonite (saponite) has been given as 9.16 Å. Thus, the x-ray data suggest that montmorillonite-chlorite is Mg-rich.

The chloritic character of the mineral was further confirmed by acid dissolution. The mineral is slightly soluble in cold 1:1 HCl but readily soluble in warm acid. Treatment with warm $1N$ HCl for a short period markedly reduced the heights of the diffractometer peaks of the montmorillonite-chlorite while the 3.53 Å peak of kaolinite and the 9.9 Å peak of mica were more clearly revealed.

Variations in the c parameter of the montmorillonite-chlorite with water loss were determined from diffractometer traces of oriented specimens in atmospheres of room air and dry air, respectively, after heating to temperatures in the range of 85° C. to 700° C. Diffractometer patterns illustrating the characteristic changes are reproduced in Fig. 1. Spacings corresponding to the reflection peaks (Table 2) are tentatively associated with integral orders of basal reflection. The mean lattice spacing derived for each temperature is no more than an approximation for a lattice rendered partially inhomogeneous by dehydration. However, the natural material in equilibrium with room air and the fully dehydrated material probably have regular layer successions.

Significant changes in the c parameter and in the reflected intensities occur on heating as shown in Table 2 and Fig. 1, respectively. In the range from 85° C. to 400° C., the basal spacings decrease from about 29 Å to 24 Å and the first order reflection disappears provided the sample is kept in dry air after heating. Under normal atmosphere conditions the mineral rehydrates very rapidly to give a first order basal spacing of about 29 Å similar to that of the unheated material. From 500 to 700° C. the first order basal reflection reappears with a spacing of about 20–22 Å while the higher orders yield a value of 23.8 Å. Thus, montmorillonite-chlorite behaves in a manner analogous to that of the chlorites in that it shows modified basal intensities after partial dehydration. In addition to these changes, the reflection peaks associated with kaolinite disappears at 600° C. confirming the presence of this mineral in the sample.

The decrease of the basal spacing from 29.1 Å to 23.8 Å, or of 5.3 Å, corresponds to a loss of roughly two water layers per unit cell. If one

chlorite layer, 14.2 Å, is subtracted from each of these parameters, the values obtained, 14.9 Å and 9.6 Å, respectively, are in good agreement with the values for air-dry and dehydrated montmorillonite. Saturated with water vapor, the mineral has a spacing of about 32 Å corresponding to approximately three layers of water.

TABLE 2. BASAL REFLECTIONS FROM NATURAL, GLYCEROL SOLVATED AND HEAT TREATED
SAMPLES IN DRY AIR OF THE <.5μ FRACTION CONTAINING
MONTMORILLONITE-CHLORITE

(Filtered CuKα Radiation, λ1.5418 Å)

n	Natural d/n	d(001)	85° C. d/n	d(001)	200° C. d/n	d(001)	300° C. d/n	d(001)	400° C. d/n	d(001)
1	30.5	30.5								
2	14.5	29.0	13.5	27.0*	12.8	25.6*	12.6	25.2*	12.4	24.8*
3	9.7	29.1	8.59	25.8	8.08	24.2	8.04	24.1	7.87	23.9
4	7.25	29.0			5.87	23.5	5.91	23.6	5.91	23.6
5			4.91	24.6	4.78	23.9	4.78	23.9	4.76	23.8
6	4.85	29.1			3.95	23.7			3.88	23.3
7			3.52	24.6	3.43	24.0	3.39	23.7	3.40	23.8
8	3.64	29.1			2.94	23.5	2.92	23.4	2.96	23.7
9										
10	2.93	29.3								
Mean d(001)		29.1		25.0		23.8		23.7		23.7

n	500° C. d/n	d(001)	600° C. d/n	d(001)	650° C. d/n	d(001)	700° C. d/n	d(001)	Glycerol d/n	d(001)
1	21.6	21.6*	22.1	22.1*	21.3	21.3*	20.1	20.1*	32.7	32.7*
2	12.1	24.2*	12.0	24.0	11.8	23.6	11.6	23.2	16.1	32.2
3	7.97	23.9	7.97	23.9	8.00	24.0	8.08	24.2	9.9	29.7 m
4	5.91	23.6							8.01	32.0
5	4.77	23.8	4.87	24.3	4.84	24.2	4.86	24.3		
6									5.34	32.0
7	3.38	23.7	3.36	23.5	3.36	23.5	3.31	23.2	4.60	32.2
8	2.96	23.7	2.96	23.7	2.96	23.7	2.94	23.5		
9									3.56	32.0
11									2.91	32.0
16									1.997	31.0
Mean d(001)		23.7		23.9		23.8		23.7		32.0

* = reflections excluded in taking mean d(001).
m = probably a mica reflection.

Further indication of the presence of montmorillonite layers was obtained by glycerol solvation which expands the c-parameter to 32.0 Å. On subtracting 14.2 Å for the chlorite, one obtains 17.8 Å for the glycerol-montmorillonite complex.

Detailed consideration of lattice structure is necessarily restricted to
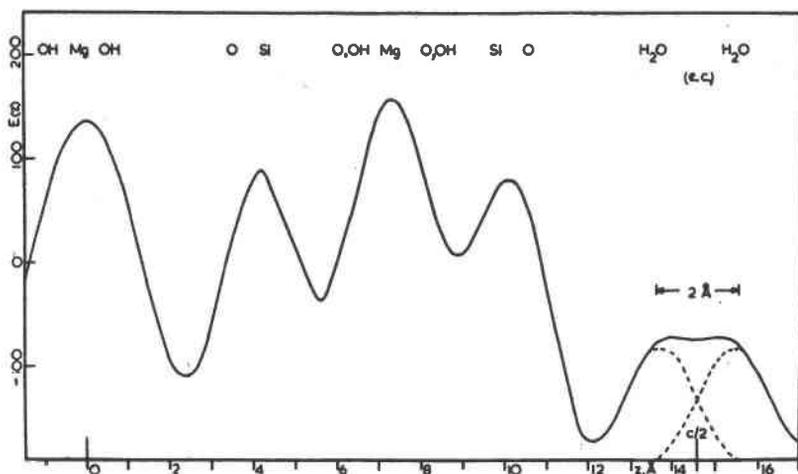
FIG. 2. Electron distribution normal to (001) of montmorillonite-chlorite.

the layer sequence in the *c*-direction. The calculated structure factors are given in Table 3. The reflected intensities were measured by integrating the peak areas of the diffractometer records for well-oriented layers. Structure factors were then calculated on the assumption that a well-oriented layer could be regarded as an extended face of a single crystal having mosaic texture. A counting technique to obtain more accurate

TABLE 3. COMPARISON OF *F* (EXP.) WITH *F* (CALC.) VALUES OF THE MONT-
MORILLONITE-CHLORITE MINERAL FROM <1μ MATERIAL

Order of Basal Reflection	Natural			Glycerol Solvated		
	I	*F* (exp.)	*F* (calc.)	*I*	*F* (exp.)	*F* (calc.
1	668	47	+35	516	49	+50
2	1,370	67	−60	616	54	−47
3	266	32	+20	16*	9	− 7
4	286	39	+20	312	44	+38
5			+14			− 3
6	170	42	+42	34	19	+35
7	10	10	+14	120	38	+37
8	284	56	+55			0
9	18	15	+22	298	69	+72
10	104	38	+65			+ 6
11				72	38	−47
16				54	42	+30

* Mica contribution not subtracted.

intensities was not worthwhile since the reliability of the experimental
F values depends on the extent of justification in applying to the oriented
layer a formula derived for a mosaic crystal.

The observed and calculated F values are compared in Table 3. The
observed values, which are relative, have been scaled so that $\Sigma|F|$ is the
same for the observed as for the calculated values. The agreement of the
observed and calculated values leaves little doubt that the structural
model is essentially correct.

Fourier syntheses of electron density were carried out using the ob-
served F values and the calculated signs given in Table 3. The electron
density curve (Fig. 2) shows clearly the alternating layers including the
brucite layer of chlorite and the interlayer of montmorillonite with two
layers of water. The individual atomic layers are not resolved by the
Fourier synthesis because the highest order which can be recorded is
00.10 with $d/n = 2.93$ Å. The unresolved peak for the two water layers
can be tentatively separated into two peaks about 2 Å apart (see Fig.
2) and this agrees with the results of Mathieson and Walker (1954)(5)
for the water layers in vermiculite; they give a separation of 2.14 Å.

<center>DEHYDRATION MEASUREMENTS</center>

A dehydration curve of the $<0.2\mu$ fraction of montmorillonite-chlorite
was obtained with the apparatus described by Earley, Milne, and Mc-
Veagh (1953)(6) using a 0.1 gram sample of air-dry material heated at
10° C. per minute to 975° C. A plot of per cent water versus temperature
(Fig. 3) shows two distinct water loss reactions corresponding respective-
ly to dehydration of the brucite and octahedral layers. In addition, a
low temperature loss of water is observed similar to that shown by all
montmorillonite type minerals. The problem of estimating the relative
proportions of montmorillonite- and chlorite-type layers in montmoril-
lonite-chlorite from the magnitudes of the water losses is rendered diffi-
cult and inexact by the same difficulty which arises in determining the
amount of structural water in a montmorillonite, namely, that a sharp
distinction cannot be made between the low temperature water (mainly
surface adsorbed water and water of cation hydration) and the structural
or hydroxyl water associated with the octahedral layers. It can be shown,
however, that the water losses are broadly consistent with the proposed
1:1 ratio of montmorillonite- and chlorite-type layers. Supposing that the
low temperature water is fully driven off by 250° C., then the remaining
water corresponds to 9.54 per cent of the sample weight at 250° C. If
300° C. is taken as the limit for low temperature water, then the remain-
ing water corresponds to 9.26 per cent of the sample weight at this tem-
perature. In both cases, the values derived from Fig. 3 are so close to the

theoretical value (9.65 per cent) for a 1:1 mixture of magnesian-chlorite and magnesian-montmorillonite that there can be little doubt as to the general correctness of the interpretation.

If an attempt is made to estimate the separate water losses, then we encounter again the same kind of difficulty because the dehydration curve
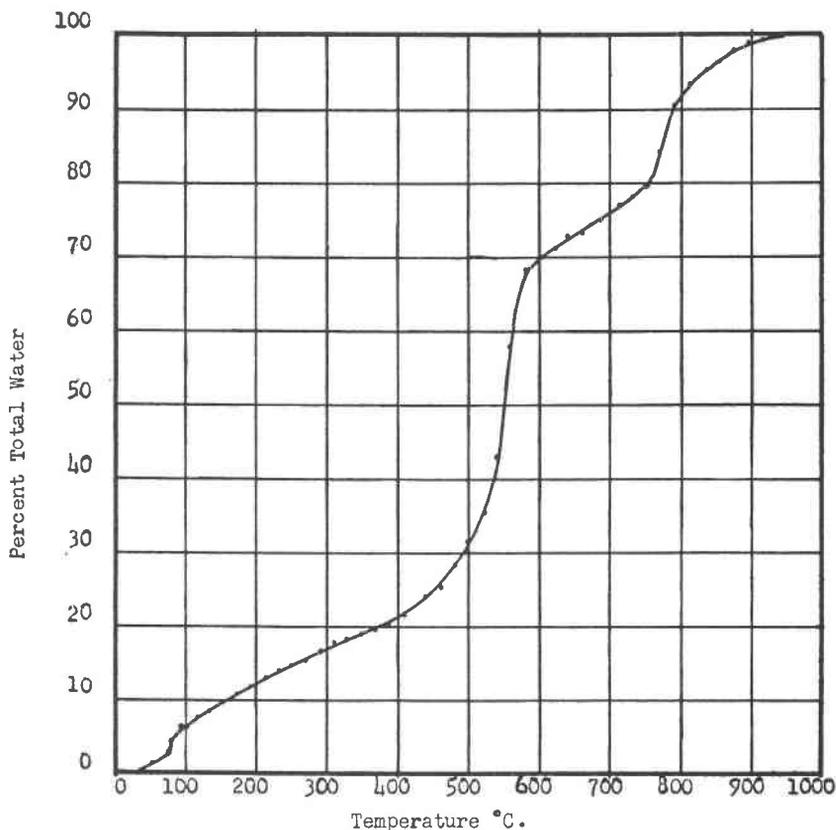
Fig. 3. Dehydration curve of montmorillonite-chlorite, $<0.2\mu$ fraction of Yates siltstone.

does not become horizontal between the two main reactions. While the end of the first reaction can be taken fairly reliably at or near the end of the first steep rise, it is very probable that the second reaction has already commenced. The uncertainty attached to any arbitrary separation of the two water losses is such that their estimation would not provide any additional valid evidence for the 1:1 montmorillonite-chlorite sequence of layers.

Differential Thermal Analysis

Differential thermal curves were obtained by heating crude, $<2\mu$ and $<0.2\mu$ air-dried materials from room temperature to 1000° C. at 10° C. per minute using apparatus described by McConnell and Earley (7). Although there are minor differences in the curves from one sample to another, the dominant endothermic peaks occur at 135° C., 215° C., 630° C., 830° C. and an exothermic peak at 850° C. In addition to the endotherms at 630° C. and 830° C. which are characteristic of brucite and octahedral layer water in chlorite, the reactions at 135° C. and 215° C. indicate interlayer water and water of cation hydration, respectively, similar to montmorillonite. Since the high temperature thermal effects of dioctahedral montmorillonites are missing, the montmorillonite

TABLE 4. CHEMICAL ANALYSIS* OF THE $<0.5\mu$ FRACTION CONTAINING
PRIMARILY MONTMORILLONITE-CHLORITE

	Per Cent		Per Cent
SiO_2	43.1	MgO	17.65
Al_2O_3	16.6	Na_2O	0.52
Fe_2O_3	6.32	K_2O	2.72
TiO_2	0.73	CO_2	0.81
MnO	0.03	H_2O	7.40
P_2O_5	0.26	C	3.40
CaO	0.94	S	0.00
		Total	100.48

* Analyst, B. B. Osthaus, Gulf Research & Development Company, Pittsburgh, Pennsylvania.

layers of montmorillonite-chlorite are probably trioctahedral as suggested by the 830° C. endotherm. The exotherm at 850° C. is attributed to the reorganization of lattice layers.

Thus, the differential thermal data substantiate the interpretation of this mineral as containing a mixture of chlorite- and montmorillonite-type layers, in agreement with the x-ray and dehydration results.

Chemical Analysis

A chemical analysis of the $<0.5\mu$ fraction of the Yates siltstone is given in Table 4.

Although some of the iron may be divalent, the total iron is expressed as trivalent because there is no analytical method for distinguishing between divalent and trivalent iron in the presence of organic matter. The CO_2 content of the sample is undoubtedly due to admixed dolomite

since x-ray diffraction lines of dolomite are present. Based on this interpretation, the sample contains 1.7 per cent dolomite. The high MgO content lends support to the presence of a chlorite-type layer while the presence of 2.72 per cent K_2O suggests potash montmorillonite and/or micaceous material. Since x-ray diffraction lines of mica are present in the pattern of this fraction, the potash is very likely associated with the mica. In view of the impurities suggested by the chemical analysis and indicated by the x-ray and thermal data, calculation of a precise chemical formula for montmorillonite-chlorite would be meaningless.

NOMENCLATURE

The question whether this mineral should have a distinctive name is worthy of consideration. Lippmann (4) has proposed the name "corrensite" for the swelling chlorite mineral which he described. However, Dr. R. C. Mackenzie, in a private communication (to G. W. B.) has expressed certain views at present under consideration by the British Clay Minerals Group† and it would be in accordance with these views to use a term such as montmorillonite-chlorite for a roughly 1:1 *random* interstratification of the two kinds of layers and a special name for a mineral in which there is a regular interstratification.

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† These discussions have now been published. See G. Brown, Report of the Clay Minerals Group Sub-Committee on nomenclature of clay minerals, *Clay Min. Bull.*, **2**, 294–302 (1955).