# **DIOCTAHEDRAL CHLORITE**<sup>1</sup>

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#### Abstract

The clay fraction from the surface soil of the Alberni soil series was found to consist predominantly of a high Al, dioctahehral chlorite. Its x-ray pattern showed a rather strong, sharp sequence of 14/n Å basal spacings and an (001) reflection which did not change position and which increased in intensity when the specimen was heated at 550° C. The (hkl) reflections showed close similarities to those of cookeite, a lithium aluminum leptochlorite.

Chemical analyses gave 40 per cent SiO<sub>2</sub>, 34 per cent Al<sub>2</sub>O<sub>3</sub>, 4.5 per cent Fe<sub>2</sub>O<sub>3</sub>, 4.5 per cent MgO, and 13 per cent H<sub>2</sub>O. The x-ray results and an Osthaus dissolution curve both resulted in a value of one tetrahedral Al per half cell. Calculation of an approximate structural formula gave

 $(Al_{3,2}Fe_{0,4}Ti_{0,1}Mg_{0,8})(Al Si_3) O_{10} (OH)_8(K_{0,2}X_{0,2}).$ 

The clay fraction of the underlying material consisted of a 40 per cent chlorite -60 per cent montmorillonite, random mixed-layer assemblage. The evidence suggests that the Al chlorite in the surface soil was derived from this type of clay.

## INTRODUCTION

Nearly all known members of the chlorite group of layer silicate minerals are trioctahedral, having magnesium and ferrous iron filling the available octahedral positions in both the mica-like sheet and the inter-layer brucite sheet. Grim (1953) states, however, that some chlorites in sediments may be dioctahedral, and Brindley & Gillery (1956) have predicted the x-ray characteristics of such minerals. There is evidence (MacEwan, 1949; Brown, 1953; Hathaway, 1955; Rich & Obenshain, 1955; Klages & White, 1957; Tamura, 1958) of 14 Å layer silicates in clays which, on heating, show x-ray reflections intermediate between 10 and 14 Å. In certain cases (Klages & White, 1957; Rich & Obenshain, 1955; Tamura, 1958) this behaviour was attributed to Al in the interlayer spaces, whereas Hathaway (1955) has suggested that organic matter may have been partly responsible. Sudo & Kodama (1957) have

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reported a high aluminum 1:1 mixed-layer mineral of montmorillonitechlorite with an (060) reflection at 1.506 Å. Their calculated formula for the mixture was

 $(Na,K,Ca/2)_{1,36}(Mg_{3,19}Al_{2,32})(OH)_{12}Al_8(Si_{13,30}Al_{2,70}) O_{40}(OH)_8 + 8H_2O$ 

indicating that both the montmorillonite and the chlorite were dioctahedral in character. However, as far as the authors are aware, a pure dioctahedral chlorite has never been reported.

Recently, an examination was made of the clay fraction of the 0- to 16inch AB horizon of the Alberni soil series, a member of the Concretionary Brown Soil Group in British Columbia. It consisted of a dioctahedral Al chlorite in sufficient purity for its properties to be determined, and these properties are described herein. The underlying C horizon of the soil consists of a mixed-layer montmorillonite-chlorite and its relationship to the AB horizon clay is discussed.

#### METHODS

The 2- to 0.2-micron and <0.2-micron clay fractions were isolated by combined sedimentation and centrifugation following destruction of organic matter with H<sub>2</sub>O<sub>2</sub>, removal of the basic cations by exchange with weak HCl, and dispersion with NaOH. Free iron oxides were then removed from a portion of the clay with sodium citrate-buffered sodium dithionite, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (Aguilera & Jackson, 1953), and this portion will be referred to subsequently as "treated" clay.

Prior to analysis by standard techniques for minerals, a portion of the "treated" sample was saturated with  $NH_4^+$  so that the exchangeable ions would not be included in the analysis. The cation exchange capacity was determined by the conductometric titration technique of Warkentin (1957).

All x-ray diffraction data were obtained with Fe-filtered Co radiation  $(\lambda = 1.78890 \text{ Å})$ . Oriented specimens of the Ca-saturated clay prepared by sedimentation on glass slides were irradiated following air-drying, ethylene glycol treatment and several consecutive heat treatments.

Differential thermal analysis curves were obtained with equipment and operating conditions described previously (Morita & Rice, 1955).

## **RESULTS AND DISCUSSION**

### X-ray Diffraction

X-ray diffraction data from 117-mm. camera films of randomlyoriented specimens of the two <0.2-micron clays are shown in Table 1 with the weak quartz reflections omitted. For comparative purposes,

(	Cookeite		A B horizon C horizon		on	
hkl	đ	I	d	I	d	Ι
			14.15	10	14.65	10
					10.16	1
					9.46	1
					8.45	1
002	6.9	<b>5</b>	7.112	<b>5</b>	7.186	<b>2</b>
					6.808	1
					6.387	1
003	4.67	7	4.784	1	4.943	1
					4.605	$\frac{2}{2}$
020	4.48	- 4	4.477	9	4.477	4
					4.157	1
					4.037	2
					3.895	ļ
004	0 50	0	0 807	-	3.792	1
004	3.52	9	3.537	5	3.009	2
			9 901	1	3.007 9.100	3
			3.201	1	3.190	4
					2.990	1
005	9.91	7	9 824	1	2.904	1
000	2.01	•	2.001	T	2.808	1
			2 716	1	2 723	î
			2.644	i	2.647	1
			2.011	1	2.595	â
201.131	2.57	9	2.569	б	2.554	4
202	2.51	Ř	2.519	ĭ		-
			2.443	$\bar{2}$	2.448	<b>2</b>
006	2.32	10	2.383	3	2.385	<b>2</b>
040	2.22	1	2.261	1	2.275	1
					2.057	1
007	2.02	3	2.006	<b>2</b>	2.008	1
135	1.96	8	1.970	1	1.897	1
206	1.86	1			1.852	1
008	1.80	<b>2</b>			1.798	1
240,150	1.69	4	1.714	<b>2</b>	1.703	1
. 009	1.538	4		~	4 405	
060	1.491	9	1.496	$^{2}$	1.499	3

TABLE 1. X-RAY DIFFRACTION DATA FROM POWDER SPECIMENS OF ALBERNI AB AND CHORIZONS<0.2 MICRON CLAY AND OF COOKEITE (ZVYAGIN & NEFEDOV, 1954)</td>

the diffraction data for cookeite, a Li-Al chlorite, published by Zvyagin & Nefedov (1954), is also included. The sequence of 14/n Å basal reflections of the AB horizon clay suggested a chlorite structure. The *b* dimension was derived from the three (0k0) reflections and was found to be 8.99 Å. This value is in accord with that usually associated with dioctahedral layer silicates (Brindley & MacEwan, 1953).

The data for the C horizon material was, in general, similar to that of the AB horizon. The b value suggested that this material also had dioctahedral characteristics. The reflections not shown by the AB horizon material may be attributed to mica, feldspar and perhaps amphiboles and pyroxenes.

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FIG. 1. X-ray diffraction patterns of oriented specimens of the Alberni AB horizon clay fractions following the Na citrate - Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> treatment of Aguilera and Jackson (1953).

Diffractometer patterns of oriented specimens of the AB horizon clays (Fig. 1) gave more conclusive evidence of the presence of chlorite. The sequence of 14/n Å reflections remained unchanged after glycol treatment and after mild heat treatment. At 550° C, the (001) peak became more intense as the higher orders began to disappear. These effects, which were more sharply defined in the patterns of the coarse than in those of the fine clay, are characteristic of chlorite.

Beginning at 300° C some of the 14 Å material appeared to collapse, giving a band of reflections between 10 and 14 Å. The nature of this apparent mixed-layer assemblage is somewhat obscure because the peak decreased gradually in *d*-spacing as the temperature was raised. It is not clearly evident from Fig. 1, but judging from a number of observations on heated fine and coarse clay, the final *d*-spacing was 11.5 Å in all cases. This corresponded to a mixed-layer in which 40 per cent was



FIG. 2. X-ray diffraction patterns of oriented specimens of the Alberni C horizon fine clay fraction following the Na citrate - Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> treatment of Aguilera & Jackson (1953).

14 Å and 60 per cent 10 Å material (Jonas & Brown, 1959). Examination following prolonged treatment with boiling weak HCl indicated the absence of kaolinite. Thus, there were two major components in this clay, a heat-stable dioctahedral chlorite and a mixed-layer chlorite and non-chlorite assemblage.

Brindley & Gillery (1956) have calculated structure factors for a number of ideal chlorite compositions and it was of interest to compare this chlorite with them. Consequently, integrated intensities, derived from step scanning of the five (00l) orders of the 2- to 0.2-micron clay, were converted to structure factors. Corrections were applied for the thickness of specimen, absorption, and degree of parallel orientation. These structure factors did not correspond either to those cited by Brind-

ley & Gillery or to those of any other combination or distribution of octahedral Al, Mg, or Fe. The most attractive explanation of this behaviour is lattice disorder arising either through mixed-layering of completely hydrated layers or through defects in the inter-layer material. These cannot be extensive because the chlorite showed a heat stability characteristic of well-ordered chlorites.

The (001) spacing of chlorites has been correlated with the number of Al atoms replacing Si in the tetrahedral layer (Brindley & Gillery, 1956) according to the equation d(001) = 14.50 - 0.31x, where x is the number of Al atoms in tetrahedral position. The average (001) spacing obtained by step-counting over the first four basal reflections of the AB horizon 2- to 0.2-micron clay was found to be  $14.19 \pm 0.02$  Å. Solution of the equation using the measured (001) spacing gave a value of x = 1.00. Thus, a tetrahedral composition of (Si<sub>3</sub>Al) is indicated.

The diffractometer patterns of the C horizon <0.2-micron clay are shown in Fig. 2. The main feature is a rather intense peak at 14.5 Å which shifted to 15.5 Å after glycol saturation. After heat treatment this peak shifted gradually to 11.5 Å. These are characteristics of a 40 per cent chlorite – 60 per cent montmorillonite random mixed-layer structure (Jonas & Brown, 1959). A small 10 Å mica peak and weak chlorite, higher order, basal spacings were shown at low temperatures, and a small chlorite (001) peak was revealed on heating at 500° C. The glycol treatment yielded a small 17 Å montmorillonite peak. Thus, the major component was a random mixed-layer 40 per cent chlorite – 60 per cent montmorillonite associated with small amounts of discrete chlorite, mica, and montmorillonite.

# Differential Thermal Analysis

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The DTA patterns of the "treated" AB horizon <0.2-micron clay are shown in Fig. 3. The samples run in air and in N<sub>2</sub> both showed the initial loss of adsorbed water at 140° C, a much smaller endothermic peak at 300° C possibly due to the dehydration of gibbsite, the loss of the major portion of lattice hydroxyls at 550° C, and an exothermic peak at 910° C due to the energy released upon recrystallization.

The broad exothermic peak at 350° C when run in air was decreased when the atmosphere was  $N_2$ . This decrease was interpreted as the suppression of the oxidation of organic matter remaining from the  $H_2O_2$ treatment. The sample run in  $N_2$  also showed a broadening of the 550° C peak, an endothermic peak at 770° C, and an increase in intensity of the 910° C peak. Although no reasonable explanation can be offered for the latter effects, it is possible that pyrolysis of organic matter may be responsible. Chlorites normally show double endothermic peaks with one



FIG. 3. Differential Thermal patterns of the treated Alberni clay run in an atmosphere of air and of  $N_2$ .

at 500-600° C due to the decomposition of the brucite layer and a smaller peak at 700-800° C due to the loss of hydroxyls from the mica portion of the structure (Caillère & Hénin, 1957). X-ray examination of the fired materials showed them to be a mixture of mullite and a spinel.

## Chemical Analyses

The total analysis of the "treated" AB horizon <0.2-micron clay is shown in Tables 2 and 3. Since the Al<sub>2</sub>O<sub>3</sub> content was high and the MgO and Fe<sub>2</sub>O<sub>3</sub> content was low, it was concluded that the dioctahedral characteristics of the chlorite are due to Al. The Li content was found to be less than 0.001 per cent. A portion of the SiO<sub>2</sub> originated in the quartz detected by x-ray diffraction. Because of the significant K<sub>2</sub>O content, it might be expected that illite or feldspar would be present, although there was no conclusive evidence of either on the basis of the x-ray data. Consequently, it was decided in the absence of any other information to carry out the following calculations on the assumption that K was fixed in the inter-layer positions. The cation exchange capacity 35.7 me./100 gm., was rather high for chlorites and this is probably due to the contribution of the mixed-layer structure. Analysis of the extract obtained

<u></u>	% of oven- dry weight	Equivalents or charges/100 gm.	Equivalents or charges/unit cell	Atoms/unit cell
$\begin{array}{c} Total SiO_2 \\ Total Al_2O_3 \\ Quartz SiO_2 \\ Tetr. SiO_2 \\ Tetr. Al_2O_8 \\ Octa. Al_2O_8 \\ Octa. Al_2O_3 \\ TiO_2 \\ MgO \\ CaO \\ K_2O \\ H_2O \\ C.E.C. \end{array}$	$\begin{array}{c} 39.85\\ 33.52\\ f=14.85\\ e=25.00\\ 9.10\\ 24.42\\ 4.56\\ 1.03\\ 4.58\\ 0.15\\ 1.61\\ 13.18\\ 35.7 \text{ me.} \end{array}$	y = 1.6642 0.5355 1.4370 0.1713 0.0516 0.2272 0.0053 0.0342 0.0357 $x = 2.4978 + 1000$	d = 11.1964 $a = 3.6027$ $9.6677$ $1.1525$ $0.3471$ $1.5285$ $0.0356$ $0.2301$ $0.2402$	$\begin{array}{l} c = 2.7991 \\ b = 1.2009 \\ 3.2226 \\ 0.3842 \\ 0.0868 \\ 0.7643 \\ 0.0178 \\ 0.2301 \\ 9.8433 \\ 0.2402 \end{array}$
			· · · · · · · · · · · · · · · · · · ·	

TABLE 2.	CALCULATION	OF THE	CHEMICAL	FORMULA	OF THE	<0.2-Micron	FRACTION
		OF T	HE ALBERN	и АВ Но	RIZON		

 TABLE 3. CALCULATION OF THE CHEMICAL FORMULA OF THE 
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 0F THE ALBERNI AB HORIZON

	Atoms/unit cell	Charges/unit cell	Net charge
Tetrahedral laver			
Si	2.7991		
Al	1.2009		-1.2009
Total	4.0000		
Octahedral lavers			
Al	3.2226	9.6677	
Fe	0.3842	1.1525	
- Îi	0.0868	0.3471	
Ŵø	0.7643	1.5285	
Total	4.4578	12.6958	+0.6958
External cations			
Ca	0.0178	0.0356	
ĸ	0.2301	0.2301	
$\widehat{\mathbf{N}}\mathbf{H}(\mathbf{C},\mathbf{E},\mathbf{C})$	0.2402	0.2402	
Total		0.5059	+0.5059
1.000			+0.0008
Formula			•
(Ale of Fe of Ti on M	(g. re) (Al anSia sa) O10	$(OH)_{8}(Ca M K_{23}X_{24})$	

during the dithionite-citrate treatment showed it to contain 10.5 per cent  $Fe_2O_3$ , 4.27 per cent  $Al_2O_3$ , and 0.94 per cent MgO. The free iron oxide content was high and removal from the sample was complete as judged by the reduction of the natural reddish-brown colour.

# Calculation of the Structural Formula

In the calculation of the structural formula of a chlorite, it was assumed as is customary, that the half cell contained 18 oxygens of which eight were present as hydroxyls. The net number of negative charges to be



FIG. 4. Dissolution curve of the Alberni fine clay by the Osthaus method (1956).

balanced by metallic cations was therefore 28. The nature of that portion of the AB material which showed gradual collapse on heat treatment is obscure, but it would probably have a deficiency of hydroxyls in relation to the ideal chlorite structure. The assumption of 28 equivalents of negative charge would then be in error. Nevertheless, it was considered that the calculation was merited for establishing an approximate chemical formula.

Before the structural formula of the chlorite could be calculated, a correction for free  $SiO_2$  had to be applied. This was accomplished by determining the amount of tetrahedral Al, by filling the tetrahedral layer with Si, and then by assigning the remaining Si as quartz or amorphous  $SiO_2$ . It has been shown above that the number of tetrahedral Al ions, calculated from the (001) spacing, was 1.00 per half cell. An attempt was made to confirm the tetrahedral Al value by the acid dissolution method of Osthaus (1956). Ten 0.2-gm. samples of clay were

treated with 30 per cent HCl in a boiling water bath for varying periods of time and then analyzed for soluble Al. When the logarithm of the undissolved Al was plotted vs. time (Fig. 4), the initial portion of the plot was a steep curve which levelled off to a straight line at a time of 3 hours. Extrapolation of this straight line to zero time gave a value of 9.1 per cent Al<sub>2</sub>O<sub>3</sub>, which was interpreted as tetrahedral Al (Osthaus 1956). The initial decomposition was too rapid in this experiment to allow a possible separate determination of inter-layer and mica-layer Al. However, getting the tetrahedral Al<sub>2</sub>O<sub>3</sub> content was the objective and was sufficient for the calculation.

The elemental analyses were reduced to charges or equivalents per 100 gm. (Table 2, Col. 2) and the tetrahedral Si content was assigned the value of y. The sum of the charges /100 gm. (x), which included the cation exchange capacity, was 2.4978 + y. Since there are 18 oxygens of which 8 are hydroxyls in the ideal chlorite half cell, the number of negative charges balanced by metallic cations is 28. The equivalents of tetrahedral Al/100 gm. were converted to equivalents/unit cell by multiplying by a factor  $K = \frac{28}{x}$ . The values of x and y were determined as follows using the notations shown in Tables 2 and 3: a, the equivalents of tetrahedral Al/unit cell, =0.5355K; b, the atoms of Al/unit cell, =a/3; c, the atoms of Si/unit cell, =4-b; d, the equivalents of Si/unit cell, =4c; y, the equivalents of Si/100 gm., =d/K. These relationships were solved for x and y and it was found that there were 1.20 tetrahedral Al atoms. The excess  $SiO_2$ , f, was 14.85 per cent. This value is rather high as judged by the x-ray data for quartz but it is possible that some of the free  $SiO_2$ may have been x-ray amorphous.

The atoms/half cell of the other elements were calculated in the usual fashion. The resulting structural formula, in which the atoms of the two octahedral layers are combined, is

$$\begin{array}{rcl} (\mathrm{Al}_{3.22}\mathrm{Fe}_{.38}\mathrm{Ti}_{.09}\mathrm{Mg}_{.76})(\mathrm{Al}_{1.20}\mathrm{Si}_{2.80}) & \mathrm{O}_{10}(\mathrm{OH})_{8}(\mathrm{Ca}_{.02}\mathrm{K}_{.23}X_{.24}). \\ & +.6958 & -1.2009 & +.5059 \end{array}$$

For comparison, when the number of tetrahedral Al ions was set equal to 1, the calculated formula was

$$\begin{array}{ccc} (\text{Al}_{3,21}\text{Fe}_{.37}\text{Ti}_{.08}\text{Mg}_{.73}) & (\text{Al Si}_{3}) & O_{10} & (\text{OH})_8 & (\text{Ca}_{.02}K_{.22}X_{.28}). \\ & +.5172 & -1.00 & +0.4817 \end{array}$$

In this case the calculated  $SiO_2$  was 11.7 per cent while 1 tetrahedral Al/ unit cell corresponded to 7.96 per cent Al<sub>2</sub>O<sub>3</sub>.

The formula calculated from the complete analysis, including all of the  $SiO_2$ , was

$$(Al_{3,18}Fe_{,31}Ti_{.07}Mg_{.62})(Al_{.39}Si_{3,61})O_{10}(OH)_8(Ca_{.01}K_{.19}X_{.19}).$$
(3)  
-.0144 -.3948 +.4088

This formula must be rejected because no allowance was made for the Si present as quartz, and the value of 0.39 tetrahedral aluminum atoms was not in accord with the x-ray and chemical data. In addition, it is unlikely that the two octahedral layers would have a net negative charge. It was concluded, therefore, that formula (1) or (2) represented more closely the composition of the chlorite.

There are two ways in which octahedral cations may be allocated to the mica-layer and inter-layer positions. One is a calculation of structure factors from intensity data which was shown above to be unsuccessful in the present case. The other method is based upon the relationship of the b dimension with the chemical composition. In setting up general equations for layer silicates, Brindley & MacEwan (1953) omitted the effect of inter-layer cations and considered only that of the mica-layer composition on the *b* value. They reported good agreement between calculated and observed values with chlorites. Therefore, observed b values may be compared with those calculated from models with assigned micalayer populations. Using the appropriate equation (Brindley & MacEwan, 1953), an ideal chlorite having 1 tetrahedral Al and 2 Al in the octahedral mica-layer, would have a b value of 8.97 Å. If all of the Mg, Fe, and Ti in structural formula (1) were assigned to the mica-layer, the calculated b would be 9.13 Å. Thus, the measured b value of 8.99 Å corresponds more closely to the value for the pure Al mica-layer model than to the other example.

The course of the decomposition during the Osthaus treatment was followed by examination with x-ray diffraction of samples after 15-min., 1-hour, 2-hour, and 6-hour treatments. The material quickly lost its crystallinity, and only the 15-min. sample showed chlorite features. When the material was heated to  $500^{\circ}$  C weak 10 Å and 3.33 Å reflections were shown by the samples treated for 15 minutes and 1 hour. The 2hour and 6-hour samples were essentially amorphous, but both showed very weak, broad; 10 Å features upon heating to  $500^{\circ}$  C. Thus, there may have been some preferential decomposition of the inter-layer material but there was no evidence of an expanding, 2:1-layer silicate as had been found previously by similar techniques (Brydon & Heystek, 1958).

# Relationship with Other Chlorites

Hey (1954) quotes Tschermak as dividing chlorites into two groups: Orthochlorites (Mg, Fe'')<sub>\$i</sub> and leptochlorites which are richer in trivalent ions and which often contain considerable ferric iron. The latter group has been called "oxidized chlorites" by Winchell (Hey 1954) since they fall into the orthochlorite group if the iron is all computed as ferrous iron. Hey (1954) used a division similar to Tschermak's with the arbitrary value of 4 per cent Fe<sub>2</sub>O<sub>8</sub> as the dividing line, and named the two groups orthochlorites and oxidized chlorites. Brown (1955) proposed a scheme using 3 groupings; (1) trioctahedral (orthochlorites) containing oxidized and unoxidized chlorites, (2) dioctahedral chlorites (none known) in which both the mica- and inter-layer sheets are dioctahedral, and (3) leptochlorites (cookeite), in which one of the layers is dioctahedral and the other is trioctahecral. Brindley & Gillery (1956) retain Tschermak's original definition of leptochlorite and deal with the mixed types under the dioctahedral minerals. The terminology, therefore, is somewhat confusing because of the different definitions for the term leptochlorite.

According to Brindley & Gillery (1956), the theoretical formula of dioctahedral chlorites is

$$Al_{(4+x/3)}Si_{(4-x)}Al_xO_{10}(OH)_8.$$

Since the octahedral layers will always have x/3 more than 4 Al per unit cell in order to maintain electrical neutrality, the ideal structure can be only approximately dioctahedral. The unique condition under which there could be exactly 4 octahedral atoms would require that the octahedral Al be replaced by quadrivalent cations equal in number to the tetrahedral Al. If divalent cations, A, are present the octahedral formula would be (Al<sub>4</sub> $A_{x/2}$ ), and if there are monovalent cations, B, it would be Al<sub>4</sub> $B_x$ . Aluminiferous chlorites would be expected, therefore, to have more than 4 of the 6 available octahedral spaces filled.

From Tables 2 and 3, it may be seen that the number of octahedral atoms was 4.46 of which 3.6 were trivalent Al and Fe and 0.76 were divalent Mg. Thus, the composition of the clay approaches the theoretical member with an octahedral composition of  $(Al_4Mg_{x/2})$ .

An example of a case where monovalent cations are present in the octahedral layers is the mineral cookeite. This mineral, an alteration product of lepidolite and spodumene, has been shown (Brammall *et al.*, 1937; Ginzburg, 1953; Zvyagin & Nefedov, 1954) to be a high aluminum  $(30-40 \text{ per cent Al}_2O_3)$ , low magnesium (0.04-0.6 per cent MgO), lithium  $(1-5 \text{ per cent Li}_2O)$  chlorite. It is characterized by an octahedral composition of LiAl<sub>4</sub> in the chlorite structure. If one assumes Al<sub>2</sub> in one octahedral layer and LiAl<sub>2</sub> in the other, it is apparent that the cookeite structure is mixed dioctahedral-trioctahedral.

The example of the mixed type which Brindley & Gillery used had an aluminum (dioctahedral) mica layer and a magnesium (trioctahedral) inter-layer so that the total octahedral composition was  $(Mg_{3-x}Al_{2+x})$ . Thus it is apparent that there are two possible cases where one layer has exactly 2 and the other exactly 3 cations; one in which Mg and Al are both major cations and the other (LiAl<sub>4</sub>) where Al alone is the major cation.

The problem of distinguishing dioctahedral, trioctahedral, and mixed

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structures in natural mixtures may be difficult in those cases where the structural formula cannot be calculated. Using the arguments presented above, a measurement of the (060) spacing should indicate the nature of the mica-layer portion. Some other kind of evidence, for example a leaching technique, would be necessary to establish the nature of the inter-layer.

## Relationship with Other Clay Minerals

It has been found by Stephen (1952) and by one of us (J.E.B.) that chlorites inherited in soils are readily altered to vermiculite under acid conditions. On the other hand, there is increasing evidence of the formation of "chloritic" minerals in the A horizon of a number of acid soils. These materials have been called "chloritized" vermiculite (MacEwan, 1949; Sawhney, 1958), dioctahedral analogue of vermiculite (Brown, 1953), dioctahedral vermiculite (Hathaway, 1955; Rich & Obenshain 1955), or simply chlorite-like material (Klages & White, 1957). Except for the clay from the Paxton soil (Tamura, 1958), all have an (060) spacing of 1.50 Å and hence are dioctahedral. All of the clays gave 14 Å reflections which did not expand on glycolation and which collapsed, on heating or K ion saturation, to a position intermediate between 10 and 14 Å. These features correspond to those expected from vermiculitechlorite random mixed-layering. However, in some cases (Hathaway, 1955; Tamura, 1956), heat treatments at successively higher temperature produced peaks which moved gradually from 14 Å down to 10 Å. It would appear that the chlorite phase in these cases did not have normal heat stability.

Prolonged treatment with hot KOH (Brown, 1953), Na citrate (Tamura, 1958), or NH<sub>4</sub>F (Rich & Obenshain, 1955) liberated a significant amount of Al, and allowed expansion to 17 Å on glycolation of all but the Paxton and ready collapse to 10 Å on heating or K ion saturation of all the specimens including the Paxton. Thus, these treated materials showed properties of montmorillonite. The Paxton clay (Tamura, 1958) differed from all the others in having an (060) value of 1.53 Å and in giving a non-expanded 14 Å spacing following citrate treatment. These are characteristics normally associated with trioctahedral vermiculite.

The various parent minerals in these cases were montmorillonite (Tamura, 1958), dioctahedral vermiculite (Brown, 1953; Rich & Obenshain, 1955), and vermiculite (Tamura, 1956). It would appear that "chloritized" minerals can be derived from various expanding-layer clay minerals regardless of whether they are dioctahedral or trioctahedral.

The mechanism by which these minerals are formed has been termed "partial chloritization" (MacEwan, 1949) and "alumination" (Tamura et al., 1959). It has been suggested by Rich (Sawhney, 1958) that this

involves the formation of polymerized basic alumina in the inter-layer spaces of expanding layer minerals. With the use of concentrated solutions of Al and subsequent neutralization, heat-stable chlorites have been formed from montmorillonite indicating the formation of a wellorganized, inter-layer hydroxide layer (Slaughter & Milne, 1958; Caillère & Hénin, 1947). When the Al concentration was low (saturating exchange sites only), drying prevented exchange of the Al with K and impeded collapse of the layers to 10 Å (Rich & Obenshain, 1955). Repeated saturation and drying cycles or one cycle including neutralization before drying gave a more pronounced effect. It is conceivable that a continuation of these cycles would eventually produce a stable 14 Å chlorite. As yet, none of the naturally occurring chloritized minerals has been shown to be heat stable.

In the Alberni soil, the chlorite-montmorillonite mixed-layer assemblage was found at several depths down to 84 inches and may be said to be inherited by the soil. The surface soil clay consisted of a mixture of a similar mixed-layer clay (though it showed no expansion beyond 14 Å), and a heat-stable 14 Å dioctahedral chlorite. It would appear that some of the inherited mixed-layer material had been chloritized giving a heatstable chlorite structure without the expansion properties of those of the synthetic Al chlorite of Slaughter & Milne (1958).

In soils, the cations, present in more than trace amounts, which would be expected to form hydroxides, are Al, Fe, and Mg. From their solubility products, precipitation of Mg(OH)<sub>2</sub> would be expected to take place in alkaline environments, and Al(OH)<sub>3</sub> and Fe(OH)<sub>8</sub> in acid and mildly alkaline environments. Since orthochlorites are unstable in acid soils (Stephen 1952), Jackson & Sherman (1953) suggested that chlorite could occur in different positions in their weathering sequence depending upon composition. Thus, in acid soils, conditions may be suitable for the decomposition of one kind of chlorite, for example orthochlorites, and the formation of another, for example Al chlorites. The later chloritization process could involve different expanding layer silicates; they may be vermiculites or montmorillonites and may be dioctahedral or trioctahedral.

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