

## STRUCTURAL ASPECTS OF DIOCTAHEDRAL CHLORITE

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## ABSTRACT

Dioctahedral chlorites described to date can be classified into three categories: 1) chlorites with two dioctahedral sheets and an octahedral cation total slightly greater than 4.0 per formula unit, 2) chlorites with one dioctahedral and one trioctahedral sheet and an octahedral cation total near 5.0, and 3) imperfectly crystallized specimens with incomplete interlayers.

The existence of di/trioctahedral sheets in category 2) has been confirmed by structural analysis for a particular Al-Mg specimen in powder form and for a similar chlorite interstratified with montmorillonite. The 2:1 layer portion of the structure is dioctahedral and the interlayer is trioctahedral. The layer type is IIb. Chemical analysis, structure factors, average T-O bond length of 1.65 Å, average basal O-O distance of 2.64 Å, and tetrahedral twist angle of 7.6° indicate a composition for both specimens near  $[Al_{2.0}(Si_{3.3}Al_{0.7})O_{10}(OH)_2]^{-0.7} [Mg_{2.3}Al_{0.7}(OH)_6]^{+0.7}$ . The lateral misfit that might be expected between mixed di/trioctahedral sheets has been accommodated structurally by thickening the trioctahedral sheet and thinning the dioctahedral sheet so that the mean octahedral edges are identical. Existing  $d(001)$  X-ray spacing graphs constructed to derive tetrahedral compositions for trioctahedral chlorites are not valid for dioctahedral species.

## INTRODUCTION

Although most chlorites are trioctahedral, dioctahedral species are being reported in the literature with increasing frequency. Specimens that have been called dioctahedral chlorite actually can be grouped into three different categories: (1) Chlorites with two dioctahedral sheets, *i.e.* with a pyrophyllite-like 2:1 layer and a gibbsite-like interlayer. The octahedral cation total is slightly greater than 4.0 per formula unit, primarily Al, and  $d(060)$  measures between 1.49 and 1.50 Å. (2) Chlorites with one dioctahedral sheet and one trioctahedral sheet. The octahedral cation total is near 5.0 per formula unit, and  $d(060)$  measures between 1.49 and 1.51 Å. (3) Less well-crystallized layer silicates comparable to (1) and (2) above, but with incompletely developed interlayer material. Such specimens, occurring mainly in soils and sediments, comprise the majority of reported dioctahedral chlorites. The incompleteness of the interlayer material is indicated by partial collapse of the layers on heating, expansion on solvation for some specimens, and relatively easy dissolution in sodium citrate or other reagents.

Because most specimens are fine grained, no structural details have been reported for dioctahedral chlorites previously. The present paper will consider only the best crystallized examples within the first two categories above. Systematic refinements of cell parameters from the

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powder pattern of a chlorite with di/trioctahedral sheets and the Fourier transform analysis of the same chlorite in regular interstratification with montmorillonite will be reported.

#### CHLORITES WITH TWO DIOCTAHEDRAL SHEETS

Several natural occurrences have been reported of chlorites believed to have two dioctahedral sheets. In most cases the chlorite is so intermixed with other materials that it cannot be characterized adequately. In other cases the interlayer material proves to be incomplete or unstable. Only the few examples that have been best characterized and that appear to have the most complete gibbsite-like interlayers are listed in Table 1*a*. In these specimens the substitution of Al for Si ranges from 0.7 to 1.3 per 4.0 positions. The octahedral cation total is always greater than 4.00 atoms, ranging from 4.27 to 4.4. This suggests that the positive charge on the gibbsite interlayer arises primarily from the presence of Al cations in excess of 2.0 in this sheet, in accord with the theoretical formula of  $\text{Al}_{(4+x/3)}(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_8$  given by Brindley and Gillery (1956). Some positive charge may arise also from anion vacancies or from the presence of extra protons.

The present writers have been able to study a dioctahedral chlorite of this type, kindly supplied by Professor G. Müller. The chlorite comes from a Permian sandstone in NW Germany and is to be described by Müller elsewhere. Although mixed with quartz and mica, sufficient purification could be obtained to identify the chlorite as being dioctahedral with  $d(060) = 1.49 \text{ \AA}$  and as having layers classified as the *Ia* type by Bailey and Brown (1962). A regular interstratification of an aluminous chlorite with swelling chlorite (Heckroodt and Roering, 1965) can also be identified as having *Ia* type layers from the published X-ray pattern. Although the  $d(060)$  value of  $1.49 \text{ \AA}$  suggests two dioctahedral sheets, the appreciable amount of Li present by analysis in this latter specimen also indicates a possible analogy with the *Ia* chlorite cookeite, which has both dioctahedral and trioctahedral sheets.

#### CHLORITES WITH DI/TRIOCTAHEDRAL SHEETS

Cookeite, a mineral known since 1862, is the earliest and best known example of a chlorite having one dioctahedral sheet and one trioctahedral sheet. Brammall, Leech, and Bannister (1937) give an ideal composition  $(\text{LiAl}_4)(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$  for cookeite. They allocate two Al to the 2:1 unit and  $2\text{Al} + 1\text{Li}$  to the interlayer "brucite" sheet. Dr. K. Norrish (personal communication, 1961) has computed a one-dimensional electron density projection that confirms the di/trioctahedral nature of cookeite, but suggests that the composition for his specimen should be  $\text{Al}_{1.78}\text{Li}_{0.36}$  for the 2:1 unit and  $\text{LiAl}_2$  for the brucite sheet. Bailey and

TABLE 1. DIOCTAHEDRAL CHLORITE OCCURRENCES

Reference	Occurrence	$d(060)$	$d(001)$	Structural formula	Impurities	Stability on heating	Expansion on solvation
a) Two dioctahedral sheets*							
1. Brydon, Clark, and Osborne (1961)	AB horizon Alberni soil, British Columbia hydrothermally altered acid tuffs, Kesselberg	1.496 Å	14.19 Å	$\sim(\text{Al}_{1.33}\text{Fe}^{2+}_{0.37}\text{Ti}_{0.08}\text{Mg}_{0.72})(\text{Si}_6\text{Al})\text{O}_{10}(\text{OH})_2 \times \text{X}_{0.47}$	qtz., ML	stable at 700°C	none
2. Müller (1961, 1963)	bauxite, East Pyrenees	1.491	14.22	$(\text{Al}_{1.7}\text{Mg}_{0.30})(\text{Si}_{1.4}\text{Al}_{1.7})\text{O}_{10}(\text{OH})_8$ and $\text{Al}_{1.37}(\text{Si}_{1.4}\text{Al}_{1.3})\text{O}_{10}(\text{OH})_8$	1M hydromuscovite calculated out	decr. to 13.2 Å at 700°C	n.d.
3. Caillère, Hénin, and Pobeguain (1962)		1.50	14.2	$(\text{Al}_{1.3}\text{Fe}^{2+}_{0.08}\text{Fe}^{3+}_{0.02})(\text{Si}_{1.7}\text{Al}_{1.3})\text{O}_{14}$	apertite + TiO <sub>2</sub> calculated out	n.d.	none
b) Mixed di/trioctahedral sheets*							
1. Brammall, Leech, and Bannister (1937)	cookeite variety in pegmatites	1.49	14.2	$\sim(\text{LiAl}_2)(\text{Si}_6\text{Al})\text{O}_{10}(\text{OH})_8$	pure	stable at 700°C	none
2. Bailey and Tyler (1960)	in iron ore, Tracy mine, Michigan	1.511	14.18	$\sim(\text{Al}_{1.7}\text{Mg}_{0.3})(\text{Si}_{1.4}\text{Al}_{1.7})\text{O}_{10}(\text{OH})_8$	pure	decr. to 14.0 Å at 500°C	none
3. Schultz (1963)	Triassic sediments, Colorado Plateau	1.50 to 1.51	?	$\sim\text{R}_{2.1}(\text{Si}_{1.4}\text{Al}_{1.6})\text{O}_{10}(\text{OH})_8$	qtz., feld.	stable at 550°C	none
4. Hayashi and Oinuma (1964)	hydrothermal alteration zone, Kamikita mine, Japan	1.509	14.18	$(\text{Ca}_{0.11}\text{Mg}_{0.18}\text{Fe}^{2+}_{0.70}\text{Fe}^{3+}_{0.08}\text{Al}_{1.02})(\text{Si}_{1.2}\text{Al}_{1.6})\text{O}_{10}(\text{OH})_8$	pyrite, ML	decr. to 14.0 Å at 600°C	to 14.5 Å
5. Frenzel and Schembra (1965)	hydrothermally altered arkose, Kaiserbach Valley	1.507	14.38	$(\text{Al}_{1.7}\text{Fe}^{2+}_{0.08}\text{Fe}^{3+}_{0.02}\text{Mg}_{0.37})(\text{Si}_{1.4}\text{Al}_{1.6})\text{O}_{10}(\text{OH})_2 \times \text{X}_{0.18}$	qtz., dol., feld.	n.d.	none

X = K, Na, + Ca, + exchangeable cations; R = total octahedral cations; ML = interstratified material.

\* Listed classification is that of the present writers, and not necessarily that of the original investigators.

Brown (1962) examined six cookeites and found all to be based on the *Ia* layer type. The  $d(060)$  value is 1.49 Å, which is typical of dioctahedral layer silicates and considerably smaller than the 1.53–1.56 Å range found for trioctahedral chlorites. Because dioctahedral sheets are characterized by two small octahedral sites occupied by Al and a larger, vacant site, it is believed that Li fits into this larger site in the cookeite interlayer without increasing  $d(060)$ . Cookeite is the only dioctahedral chlorite known so far to occur in single crystals. At least two different 2-layer polytypes occur and are in the process of structural refinement (Lister, 1966). The exact status of mananodite, listed by Frank-Kamenetsky (1960) as a dioctahedral Li-Al chlorite with some substitution of boron in the tetrahedral positions, is uncertain.

In 1954 Sudo and his co-workers in Japan identified an Al-Mg dioctahedral chlorite as one of the constituents of a regular interstratification of chlorite with montmorillonite. This material has now been reported from the hydrothermal alteration zones around five different ore bodies in western Japan (Sudo, 1959). The chloritic component was first described as having pyrophyllite-like and gibbsite-like sheets, *i.e.* having two dioctahedral sheets. However, allocation of a chemical analysis of pure material from the Kamikita mine (Sudo and Kodama, 1957) gives an octahedral cation total of 4.75 for the chlorite component. The allocation shown by these authors for the "gibbsite" sheet contains more Mg than Al, and is probably trioctahedral. A di/trioctahedral structure is also suggested by the  $d(060)$  value of 1.506 Å, which is rather large for a combination of two dioctahedral sheets composed only of Al.

Bailey and Tyler (1960) reported two similar occurrences in Michigan of an apparent regular interstratification of dioctahedral chlorite and montmorillonite, one from an alteration zone around an ore body and the other in fractures in an altered igneous rock. A partial chemical analysis of the former material shows slightly more MgO and SiO<sub>2</sub> than in the Kamikita material and slightly less Al<sub>2</sub>O<sub>3</sub>. The  $d(060)$  value is 1.507 Å for the Michigan material.

Bailey and Tyler also report several occurrences in Michigan of a similar chlorite in random interstratification with montmorillonite and of a non-interstratified dioctahedral chlorite. The  $d(060)$  value of the latter ranges from 1.505 to 1.511 Å in different specimens. The material does not expand on solvation with glycerol. The 001 reflection at 14.23 Å increases in intensity by a factor between four and five on heating at 500°C and decreases in spacing only to 14.0 Å. Static heating at 1000°C produces spinel and at 1200°C produces cordierite plus spinel. The ideal formulas of both products contain twice as much Al as Mg, confirming

the dioctahedral nature. It seems likely that this is the same chlorite as that in the regular and random interstratifications and that it is a second example of a chlorite with di/trioctahedral sheets. The indexed powder pattern (Table 6) indicates the layer type is *IIb*.

Schultz (1963) has described the occurrence of 20 samples of aluminous chlorite from sediments in Triassic rocks of the Colorado Plateau. The  $d(060)$  values are between 1.50 and 1.51 Å, and the 003 reflection is considerably more intense than should be the case for a trioctahedral chlorite. A chemical analysis of impure material shows slightly more  $\text{Al}_2\text{O}_3$  than  $\text{MgO}$  and, according to allocation by the present writers, yields an octahedral total near five atoms. These data suggest the presence of mixed di/trioctahedral sheets, but further details are needed for verification.

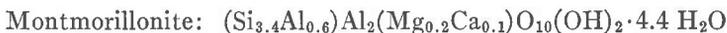
Hayashi and Oinuma (1964) report dioctahedral chlorite in the alteration zone of the Kamikita mine, Japan. The  $d(060)$  value is 1.509 Å, the  $d(001)$  value of 14.18 Å is stable on heating and solvation, and the intensity of 001 increases by a factor of five to six on heating at 600°C. Because the powder pattern is similar to that given by Bailey and Tyler, the layer type is probably *IIb*. Allocation of a chemical analysis yields the formula listed in Table 1*b*. Minor impurities of mixed-layer clay and pyrite are included in this formula. Both Schultz (1963) and Hayashi and Oinuma (1964) note that dioctahedral chlorite is more resistant to HCl than are the trioctahedral varieties.

Frenzel and Schembra (1965) have described dioctahedral chlorite from hydrothermally altered arkose in the Kaiserbach Valley. The  $d(001)$  value of 14.11 Å does not change after solvation. The X-ray powder pattern is similar to those of Bailey and Tyler (1960) and of Hayashi and Oinuma (1964), but contains impurities of quartz, dolomite, and feldspar. The  $d(060)$  value is 1.507 Å. Allocation of a chemical analysis yields 4.80 octahedral cations plus 0.13 exchangeable cations (Table 1*b*).

The evidence cited above for the existence of Al-Mg chlorites with di/trioctahedral sheets is indirect. It depends on the intermediate value of  $d(060)$ , on chemical analysis of impure material, and on the ideal compositions of the recrystallization products of static heating. The present writers have undertaken the structural refinement of the Bailey and Tyler (1960) specimens, which occur pure, in order (1) to verify the presence of di/trioctahedral sheets, (2) to determine whether the dioctahedral sheet is in the 2:1 layer or in the interlayer, and (3) to determine any structural adjustments within the layers resulting from the presence of both dioctahedral and trioctahedral sheets in the same layer. Both the dioctahedral chlorite and the interstratification of a similar chlorite with montmorillonite have been examined.

## INTERSTRATIFIED DIOCTAHEDRAL CHLORITE-MONTMORILLONITE

An apparent regular interstratification of dioctahedral chlorite with montmorillonite occurs as a fine-grained greenish coating on shear surfaces in an altered dike in the Geneva-Davis iron mine, Gogebic district, Michigan. A partial chemical analysis is listed in Table 2. Assuming that the tetrahedral sheets of the chlorite and montmorillonite have the same composition, the analysis can be allocated as follows:



The chloritic component has one dioctahedral sheet and one trioctahedral sheet.

TABLE 2. CHEMICAL ANALYSIS OF INTERSTRATIFIED CHLORITE-MONTMORILLONITE

	Wt. %
SiO <sub>2</sub>	42.15
TiO <sub>2</sub>	nil
Al <sub>2</sub> O <sub>3</sub>	28.95
Cr <sub>2</sub> O <sub>3</sub>	trace
Fe <sub>2</sub> O <sub>3</sub>	trace
FeO	nil
MgO	11.20
CaO	0.65
K <sub>2</sub> O	nil
Na <sub>2</sub> O	n.d.
H <sub>2</sub> O	n.d.

Diffraction patterns were obtained from oriented aggregates of the interstratified clay in a water-saturated state, after solvation with glycerol, and after heating at 500°C. The average basal spacing  $d(001)$  is 28.9 Å for the natural material, 32.1 Å after solvation, and 24.1 Å after dehydration. Because the  $00l$  spacings deviate slightly from integral submultiples, some deviation from exact regularity of interstratification is suggested. The observed patterns are listed in Table 3.

Fourier transforms for the solvated and heated clays were calculated according to the methods of MacEwan (1956) and MacEwan, Ruiz Amil, and Brown (1961). An average layer structure factor was used to take into account the different interlayer scattering powers in the two components. The observed peak heights obtained from the two transforms were averaged. To test the consistency of the results, theoretical peak heights for three-layer packets were calculated from the probabilities derived from the one- and two-layer packet sequences. Some dis-

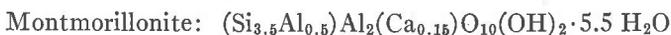
agreement was noted between observed and calculated peak heights so the transform was reevaluated as an integral, the function being summed at intervals of  $0.1^\circ \theta$ . Agreement between the observed and calculated peak heights was much closer with the integral method than with the series summation (Table 4).

The failure of the series transform to give internally consistent results can be attributed partly to the breadth of the diffraction maxima. MacEwan's derivation of the series transform assumes a rapid change in intensity for a small change in theta. The peaks from the material used in this study had appreciable intensity over a range of  $3^\circ 2\theta$ , hence the use of a Fourier series is not completely justified.

TABLE 3. DIFFRACTOMETER PATTERNS OF ORIENTED CHLORITE-MONTMORILLONITE CLAY

00l	Water slurry		Solvated		Heated 500°C	
	d	I	d	I	d	I
1	29.0 Å	100	32.7 Å	100	—	0
2	14.5	71	15.9	95	12.5 Å	100
3	9.65	8	—	0	8.065	22
4	7.27	6	8.01	23	—	0
5	—	0	—	0	4.76	35
6	4.81	22	5.330	5	—	0
7	—	0	4.622	25	3.417	30
8	3.583	10	—	0	2.965	8
9	—	0	3.546	20	—	0
10	2.889	5	—	0	—	0
11	—	0	2.902	5	—	0

The Fourier transforms show that the interstratified material is 60 percent chlorite and 40 percent montmorillonite. Reallocating the chemical analysis in these proportions gives an approximate composition:



The sample was not analyzed for sodium, and this may explain the discrepancy between the tetrahedral sheet charge and the interlayer charge in the montmorillonite component. Also, there is no requirement that the tetrahedral sheets have the same composition in both components. They are listed in this manner because of lack of evidence to the contrary.

An attempt was made to distinguish between two possible structural models for the chloritic component of the interstratified clay by means of the transform integral. Model 1 has a dioctahedral 2:1 layer and a tri-

octahedral interlayer. Model 2 has a trioctahedral 2:1 layer and a dioctahedral interlayer. Although Model 1 gives slightly more selfconsistent results than Model 2, especially for four-layer packets, the transform integral is only slightly affected by the change in distribution of cations between the octahedral sheets (Table 4).

More certain evidence for the dioctahedral nature of the 2:1 layer of

TABLE 4. FOURIER TRANSFORM PEAK HEIGHTS FOR INTERSTRATIFIED CHLORITE-MONTMORILLONITE

Packet*	Series summation		Integral method			
	Obs.	Calc.	Model 1		Model 2	
			Obs.	Calc.	Obs.	Calc.
C	57		61		60	
M	43		39		40	
CC	13		34		30	
CM	87		61		66	
MM	0		5		4	
CCC	12	3	29	22	15	15
CMC	66	64	53	57	59	60
MCM	22	33	18	20	26	25
MMM	0	0	0	1	0	0
CCCC			12	13	13	7
CMCM			35	35	54	45
CCCM			53	52	27	44
MMMC			0	0	6	4
MMMM			0	0	0	0

\* C = Chlorite, M = Montmorillonite.

the chlorite is found by comparison of observed and calculated structure amplitudes for the basal reflections of water saturated material (Table 5). The agreement is markedly better for Model 1 than it is for Model 2. Intuitively one would expect this result because it gives similar compositions to the 2:1 unit in both the chlorite and montmorillonite components. The primary difference is in the interlayers.

It is not possible to have exact alternation of different layer types if the components are present in unequal amounts. However, the probabilities of layer sequences expected for any ratio of layers in regular or random interstratification can be calculated and converted into expected peak

TABLE 5. COMPARISON OF 001 STRUCTURE AMPLITUDES FOR HYDRATED CHLORITE-MONTMORILLONITE

001	Model 1			Model 2		
	F <sub>o</sub> *	F <sub>e</sub>	F <sub>o</sub> -F <sub>e</sub>	F <sub>o</sub> *	F <sub>e</sub>	F <sub>o</sub> -F <sub>e</sub>
001	64	67	-3	68	56	12
002	79	75	4	84	96	-12
003	33	37	-4	36	46	-10
004	32	22	10	35	22	13
006	78	75	3	83	88	-5
008	63	70	-7	67	64	3
0010	52	55	-3	55	56	-1

\* Adjusted to  $\Sigma F_o = \Sigma F_e$ .

heights. Comparison of these calculated values, listed below, with the observed peak heights in Table 4 gives the unexpected result that the series approximation suggests a very regular system whereas the more rigorous integral method suggests one intermediate between regular and random. The latter result is in agreement with calculations by MacEwan and others (1961), who found that quite a modest degree of regularity can impart diffraction effects that resemble regular interstratification.

<i>Packet</i>	<i>3:2 regular</i>	<i>3:2 random</i>
CC	20	36
CM	80	48
MM	0	16
CCC	7	22
CMC	66	43
MCM	27	29
MMM	0	6

#### REFINEMENT OF DIOCTAHEDRAL CHLORITE STRUCTURE

Fine grained, whitish dioctahedral chlorite occurs disseminated in hematite ore at the Tracy mine, Michigan. It can be obtained pure, although not in amount sufficient for chemical analysis. The indexed powder pattern is given in Table 6. Cell dimensions, refined from the pattern by a least-squares procedure, are  $a = 5.237 \pm 3$ ,  $b = 9.070 \pm 5$ ,  $c = 14.285 \pm 13 \text{ \AA}$ , and  $\beta = 97^\circ 02' \pm 05'$ .

The powder pattern corresponds to that of a II*b* layer type according to the data of Bailey and Brown (1962). Regular layer stacking is indicated by the presence of a series of weak  $k \neq 3n$  reflections. Two regular one-layer polytypes are possible for this layer type, namely II*b*-2 and II*b*-4 with

TABLE 6. POWDER PATTERN DIOCTAHEDRAL CHLORITE, TRACY MINE

$d_{\text{obs}}$	$I_{\text{obs}}$	$hkl$	$d_{\text{calc}}$	$I_{\text{calc}}$	$d_{\text{obs}}$	$I_{\text{obs}}$	$hkl$	$d_{\text{calc}}$	$I_{\text{calc}}$
14.23	80	001	14.18	37	1.984	50B	204, 13 $\bar{5}$	1.983	53
7.13	70	002	7.09	52	1.868	15	20 $\bar{6}$ , 135	1.866	17
4.735	80	003	4.726	83	1.812	25B	205, 13 $\bar{6}$	1.809	27
4.517	85	020, 110	4.535		1.710	15 B	207, 136	1.702	
4.314	5	021	4.289		1.643	5 B	206, 137	1.651	
4.180	5	111	4.171		1.556	40 B	208, 137	1.555	41
4.017	5	11 $\bar{2}$	4.002		1.511	60	060, 33 $\bar{1}$	1.512	51
3.840	2	022	3.820		1.478	10	062, 331, 33 $\bar{3}$	1.478	4
3.552	65	004	3.544	60	1.439	5	063, 332, 33 $\bar{4}$	1.440	3
3.272	2	023	3.272		1.418	2	0.0. 10	1.418	3
3.084	4	113	3.102		1.389	40 B	{208, 139, 064, 333, 33 $\bar{5}$ }	1.389	
2.923	2	11 $\bar{4}$	2.943		1.331	2	065, 334, 33 $\bar{6}$	1.334	1
2.839	20	005	2.836	19	1.297	15	{400, 26 $\bar{2}$ , 40 $\bar{3}$ , 261}	1.297	16
2.783	1	024	2.798		1.274	17	{401, 26 $\bar{3}$ , 40 $\bar{4}$ , 262}	1.275	
2.606	10	{200, 13 $\bar{1}$ , 20 $\bar{1}$ , 130}	2.599	12	1.256	10			
2.544	25	20 $\bar{2}$ , 131	2.542	29	1.217	10 B	2.0. $\bar{1}\bar{1}$ ; 1.3. 10	1.215	
2.501	100	201, 13 $\bar{2}$	2.503	110	1.182	2	0.0. 12	1.181	2
2.409	50	20 $\bar{3}$ , 132	2.405	52	1.163	2	407, 265	1.169	5
2.348	25	202, 13 $\bar{3}$	2.349	26	1.129	2	2.0. $\bar{1}\bar{2}$ ; 1.3. 11	1.119	
2.230	25	20 $\bar{4}$ , 133	2.230	20	1.082	2	406, 26 $\bar{8}$	1.084	
2.160	2	042	2.159						
2.024	5	007	2.025	7					

Pattern taken in 114.6 mm camera, CuK $\alpha$  radiation, corrected for film shrinkage, intensities measured photometrically.

ideal space groups  $C2/m$  and  $C\bar{1}$  respectively. Attempts to identify which polytype is present were inconclusive; best agreement between observed and calculated intensities was obtained for a mixture of both polytypes. Because Bailey (1966) has pointed out that almost all dioctahedral layer silicates are two-layer polytypes, consideration was also given to the possibility of a two-layer polytype in which the  $k \neq 3n$ ,  $l = 2n$  reflections are much stronger than the  $k \neq 3n$ ,  $l = 2n + 1$  reflections. If one assumes a  $c$  glide plane to be present, there are only three two-layer polytypes having  $IIb$  layers. All three theoretical structures, however, predict  $k \neq 3n$ ,  $l = 2n + 1$  reflections that are not observed.<sup>1</sup>

By use of the more intense  $k = 3n$  reflections the average structure within the layer can be obtained, regardless of the sequence of layer

<sup>1</sup> After the present paper was in press, an abstract by V. A. Drits appeared in Abstracts, 7th Congr. Int. Union Crystallogr., Moscow, describing a 2-layer chlorite with di/trioctahedral sheets. The structure proposed is the same as one of the three 2-layer models considered in the present paper, except for the choice of an alternate  $Z$  direction.

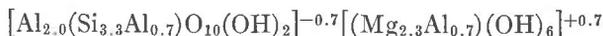
stacking. For these reflections atoms repeating at intervals of  $b/3$  are indistinguishable. Atoms of this type were grouped together and their  $y$  parameters fixed at the ideal values. The other 11 atomic parameters plus a scale factor were refined by a least-squares procedure, using a total of 47 reflections. The multiplicity of the powder lines was allowed for by distributing the observed line intensity among the contributing spectra according to the ratio calculated from the model in use. The distribution of intensity for each line was changed where necessary as refinement progressed. Reflections that make unequal contributions to a given powder line were assigned lesser weights in the least squares procedure, as were the weakest reflections. Because of the lack of evidence to the contrary, the symmetry of the average layer was assumed to be  $C2/m$ . Isotropic temperature factors were arbitrarily fixed at  $B=1.0$  for cations and  $B=2.0$  for anions.

The agreement between observed and calculated intensities is only moderately good for a structure with two dioctahedral sheets, but is very good for a structure with one dioctahedral and one trioctahedral sheet. This latter structure was tested further by running four least-squares refinement cycles for each of the two possible models of octahedral cation distribution. Model 1, which has a dioctahedral 2:1 layer and a trioctahedral interlayer, proved superior to Model 2 because of the lower reliability factor attained by refinement (weighted  $R=6.0\%$  relative to  $9.1\%$ ) and the more reasonable values of the bond lengths.

The  $X$ -ray spacing graphs in the literature that show  $d(001)$  as a function of tetrahedral composition for trioctahedral chlorites are not valid for dioctahedral chlorites. With the exception of the Caillère *et al.* specimen, analyzed dioctahedral chlorites show 0.3 to 0.6 fewer atoms of tetrahedral Al than would be expected from the  $d(001)$  values. For this reason at the start of the investigation the same tetrahedral composition was assumed for the pure chlorite specimen as found for the chloritic component in the interstratified material, namely  $Si_{3.5}Al_{0.5}$ . The average T—O bond length for this composition should be 1.641 Å according to the standard values of Smith and Bailey (1963). The refined values found in the present study are 1.655 Å for Model 1 and 1.685 Å for Model 2. From other published data the average tetrahedral basal oxygen—oxygen distance can be predicted as 2.64 Å for this composition. The refined value for Model 1 is 2.64 Å, but for Model 2 it is 2.70 Å. The angle of tetrahedral twist to be expected for this composition is  $7.5^\circ$  (Brown and Bailey, 1963). The observed values are  $7.6^\circ$  for Model 1 and  $14.7^\circ$  for Model 2.

The three criteria above indicate a mean tetrahedral composition of  $Si_{3.34}Al_{0.66}$  for Model 1 and  $Si_{2.43}Al_{1.57}$  for Model 2. The mean value for

Model 2 is unreasonable, but the mean value for Model 1 is within experimental error of the composition of  $\text{Si}_{3.26}\text{Al}_{0.74}$  found by chemical analysis of the Hayashi and Oinuma (1964) specimen, which has nearly identical  $d$ -values and intensities to the Tracy mine specimen. An over-all composition for the latter specimen of



is therefore consistent with the structural results, with the  $d$ -values by comparison with a similar analyzed specimen, and with the relative ratios of Si:Al:Mg found by analysis of the interstratified material. An attempt to obtain a quantitative analysis of the Tracy mine specimen on the University of Chicago electron probe was unsuccessful.

The final atomic coordinates for Model 1 are listed in Table 7. Bond

TABLE 7. FINAL ATOMIC PARAMETERS DIOCTAHEDRAL CHLORITE

Atom		$x$	$y$	$z$
8 T	( $\text{Si}_{0.83}\text{Al}_{0.17}$ )	.231 <sub>2</sub>	1/6	.190 <sub>9</sub>
2 M(1)	(vacant)	0	0	0
4 M(2)	(Al)	0	1/3	0
4 M(2), 2 M(4)	( $\text{Mg}_{0.77}\text{Al}_{0.23}$ )	0	1/6, 1/2	1/2
8 O (1), 4 (OH)(1)		.190 <sub>0</sub>	1/6, 1/2	.072 <sub>4</sub>
4 O (2)		.194 <sub>3</sub>	0	.236 <sub>8</sub>
8 O (3)		.506 <sub>6</sub>	.233 <sub>5</sub>	.233 <sub>2</sub>
4 (OH)(2), 8 (OH)(3)		.142 <sub>1</sub>	0, 1/3	.424 <sub>3</sub>

lengths and angles computed from these coordinates are listed in Table 8. Standard deviations are not listed because of uncertainty as to the correct weighting scheme to be used for the case of structural analysis of a powder. If the crystal has a two-layer structure, the refined  $x$  and  $y$  coordinates will be average values, and the standard deviations will incorporate the real differences from these average positions. The accuracy is probably greater than might first be assumed because (1) the refinement is of a layer type whose parameters have already been studied previously by single crystal techniques, and (2) the reflections available are primarily of type  $20l$ , which are the most useful for refining details within a layer. The internal consistency of the structure and the agreement of bond lengths and angles both within the structure and with those of similar structures suggest standard deviations not greater than 0.03 Å for bond lengths.

Use of only  $k=3n$  reflections during refinement necessarily introduces some indeterminacy into the structure because most of the  $y$  parameters cannot be varied from their ideal positions. Tetrahedral and octahedral

TABLE 8. INTERATOMIC DISTANCES AND ANGLES

(1) Tetrahedral distances in Å (* = apical oxygen)	
T—O (1)* = 1.68	O (1)*—O (2) = 2.79
T—O (2) = 1.67	O (1)*—O (3) = 2.73
T—O (3) = 1.61	O (1)*—O (3)' = 2.75
T—O (3)' = 1.66	O (2) —O (3) = 2.68
	O (2) —O (3)' = 2.61
Mean = 1.65 <sub>6</sub>	O (3) —O (3)' = 2.64
	Mean = 2.70
(2) Octahedral distances in Å († = edge shared by two octahedra)	
M (1)—O (1) = 2.02 × 4	M (2)—O (1) = 2.02 × 2, 2.03 × 2
M (1)—(OH) (1) = 2.03 × 2	M (2)—(OH) (1) = 2.02 × 2
M (4)—(OH) (2) = 2.05 × 2	M (3)—(OH) (2) = 2.05 × 2
M (4)—(OH) (3) = 2.05 × 4	M (3)—(OH) (3) = 2.05 × 2, 2.05 × 2
	around M (2)
O (1)—O (1) = 3.02 × 2, 2.69 × 2	O (1)—O (1) = 3.02 × 2, 2.69 × 2 †, 2.69
O (1)—(OH) (1) = 3.02 × 4, 2.69 × 4	O (1)—(OH) (1) = 3.02 × 2, 3.02 × 2, 2.69 × 2
	(OH) (1)—(OH) (1) = 2.69 †
	around M (4)
(OH) (2)—(OH) (2) = 2.77 †	(OH) (2)—(OH) (3) = 3.02 × 4, 2.77 × 4 †
(OH) (2)—(OH) (3) = 3.02 × 2, 3.02 × 2, 2.77 × 2 †	(OH) (3)—(OH) (3) = 3.02 × 2, 2.77 × 2 †
(OH) (3)—(OH) (3) = 3.02 × 2, 2.77 × 2 †, 2.77 †	
(3) O—(OH) distances in Å between sheets	
O (2) —(OH) (2) = 2.72 × 2	
O (3) —(OH) (3) = 2.80 × 2	
O (3)'—(OH) (3) = 2.80 × 2	
Mean = 2.77	
(4) Tetrahedral bond angles in degrees (* = apical oxygen)	
O (1)*—T—O (2) = 112.9	
O (1)*—T—O (3) = 112.1	
O (1)*—T—O (3)' = 111.0	T—O (2)—T = 130.2
O (2) —T—O (3) = 109.5	T—O (3)—T = 135.1 × 2
O (2) —T—O (3)' = 103.3	
O (3) —T—O (3)' = 107.5	Mean = 133.5
Mean = 109.4	

ordering, if present, cannot be detected. Although the space group requires that the vacant octahedral site be at  $M_1$  on the mirror plane, the reflections used require that the  $M_1$  and  $M_2$  octahedra be identical (Table 8). In reality, it may be expected by analogy with other dioctahedral structures that the  $M_1$  vacant site is larger than the occupied  $M_2$  sites, that the apical oxygens tilt away from the vacant site, and that the basal oxygen surface is corrugated. Although the basal oxygens are not precisely coplanar in the present structure, the deviation is small and is not considered to be real.

Müller (1963) states that it is questionable whether a trioctahedral

brucite interlayer can exist in combination with a pyrophyllite-like 2:1 layer because of the different lateral dimensions involved. In this specimen a structural accommodation has been reached by thickening the trioctahedral sheet considerably and by thinning the dioctahedral sheet slightly so that the lateral dimensions of the two sheets are identical. The mean lateral octahedral edge is 3.02 Å in both sheets. The brucite interlayer is thicker (2.15 Å) than in any other chlorite so far investigated (1.90 to 2.03 Å range). The dioctahedral sheet is probably as thin (2.05 Å) as such sheets can be without greatly increasing anion repulsion. The thicknesses recorded in other dioctahedral 2:1 species studied to date range from 2.04 to 2.10 Å, exclusive of celadonite, for which a value of 2.46 Å is reported.

The larger tetrahedral sheets have adjusted to the size of the smaller octahedral sheets by tetrahedral rotation and by a slight thickening. Bailey (1966) in a survey of layer silicate structures cites tetrahedral rotation angles of 7.3° to 11.3° for dioctahedral species having no substitution of tetrahedral Al for Si and values of 12.8° to 21.0° for tetrahedral compositions from Si<sub>3</sub>Al to Si<sub>2</sub>Al<sub>2</sub>. The observed angle of twist (7.6°) for dioctahedral chlorite is smaller than normally expected for its tetrahedral composition, but is appropriate when the adjusted thicknesses of the octahedral sheets are considered. The direction of twist is such as to move each basal oxygen closer to the nearest brucite OH group, as found for all other chlorites.

The thinned dioctahedral sheet is compensated by a slightly thickened tetrahedral sheet so that the total thickness of the 2:1 pyrophyllite layer (6.65 Å) is similar to those in muscovite and paragonite (6.58 Å) and to the 2:1 talc layers in other chlorites (6.64 to 6.69 Å range). Despite the thickened brucite interlayer, the *d*(001) value of 14.177 Å is smaller than would be expected for a trioctahedral chlorite of similar net layer charge. This is the case for most other dioctahedral chlorites as well. For the Tracy mine specimen with di/trioctahedral sheets, comparison of sheet thicknesses with other chlorites indicates that this smaller *d*(001) value is due primarily to a closer approach of the basal oxygens to the brucite hydroxyls. The mean perpendicular O—OH distance is 2.69 Å compared to 2.75 to 2.85 Å for trioctahedral chlorites. For chlorites with two dioctahedral sheets the additional effect of a thinner interlayer sheet may be expected.

#### GENESIS

According to Shirozu and Bailey (1965) the most stable type of chlorite layer is II*b*. This layer type is to be expected, therefore, when sufficient thermal energy is available in the environment of crystallization. Bailey

and Tyler (1960) suggest a hydrothermal origin for the Tracy mine dioctahedral chlorite because of its proximity to known dikes and close association in the ore with dickite and nacrite. The other chlorites with di/trioctahedral sheets that can be identified as IIb types, those of Hayashi and Oinuma (1964) and of Frenzel and Schembra (1965), are also described as hydrothermal in origin.

The sedimentary dioctahedral chlorite supplied to the writers by Professor Müller is the Ia layer type. Data from additional specimens will be needed to determine whether the difference noted in layer type is due to structural causes, *i.e.* because of having two dioctahedral sheets, or to its sedimentary rather than hydrothermal origin. Bailey and Brown (1962) and Shirozu and Bailey (1965) suggest that Ia and Ib layer type chlorites are high structural energy forms that may crystallize metastably and persist indefinitely within a sedimentary environment. Thus, they may be indicative of a low temperature, authigenic origin.

#### NOMENCLATURE

Chlorites with di/trioctahedral sheets pose a problem in nomenclature because they are intermediate structurally between wholly dioctahedral and wholly trioctahedral species. The Clay Minerals Group of the Mineralogical Society (London) originally proposed the term *leptochlorite* for species of this type (Brown, 1955). Cookeite was listed as the only certain representative of the di/trioctahedral group at that time. The most recent recommendation is that of the nomenclature subcommittee of the international clay organization, Comité International pour l'Étude des Argiles (C.I.P.E.A.). Their 1966 report (G. W. Brindley, pers. commun.) suggests that for the present the term *dioctahedral chlorite* should include all species with four to five octahedral cations per formula unit and that *trioctahedral chlorite* should include species with five to six octahedral cations per formula unit. Eventually, terms such as *di-tri octahedral chlorite* and *tri-di octahedral chlorite* may be used when these structural schemes can be identified clearly, the first prefix referring to the silicate sheet. The usage in the present paper is in accord with these recommendations, except that *di/trioctahedral* is preferred to *di-tri octahedral*.

Müller (1963) has proposed the name *sudoite* as a group or subgroup name for dioctahedral chlorite, assumed at that time always to have two dioctahedral sheets. Frank-Kamenetsky, Logvinenko, and Drits (1965) have proposed the name *tosudite* for a regular interstratification of dioctahedral chlorite with montmorillonite, similar to the interstratification described in the present paper. Both names are in honor of Professor T. Sudo of Tokyo University. The nomenclature committee of The Clay Minerals Society does not favor usage of specific group or subgroup

names within the chlorite series, but considers that the name *sudoite* would be suitable as a species designation (G. W. Brindley, pers. commun., 1966). The present writers propose that *sudoite* would be especially appropriate as a species name for chlorites of the type studied by Professor Sudo, *i.e.* Al-Mg specimens having IIb layers consisting of a dioctahedral 2:1 silicate unit and a trioctahedral interlayer. No names are considered necessary for interstratified materials.

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