

STRUCTURES OF INTERGROWN TRICLINIC AND MONOCLINIC *Iib* CHLORITES FROM KENYA

HONG ZHENG AND STURGES W. BAILEY

Department of Geology & Geophysics, University of Wisconsin
Madison, Wisconsin 53706

Abstract—Triclinic *Iib*-4 and monoclinic *Iib*-2 clinocllore polytypes from Kenya are intergrown laterally in (001) platelets and are separated optically in some places by sharp lines of demarcation and in other places by embayed boundaries. Electron microprobe analyses show no compositional differences between the two polytypes. Structural refinements of each show that the 2:1 layer is identical in the two structures with no tetrahedral or 2:1 octahedral cation ordering in either ideal or subgroup symmetries. The two interlayer sheets differ only in the distribution of Al and Mg over interlayer sites M3 and M4, but not in the distribution of Fe^{3+} , Fe^{2+} , or vacancies. The monoclinic *Iib*-2 polytype is less ordered than the triclinic *Iib*-4 polytype. The mean M–O,OH bond length of 1.990 Å indicates significantly less of the smaller Al present in the M4 site of *Iib*-2 than for the mean M–O,OH value of 1.957 Å for the M4 site of *Iib*-4. The textural relations and the structural refinements suggest that the monoclinic *Iib*-2 structure is inherently less stable than the triclinic form. This is in accord with the observed lesser abundance in nature of the monoclinic form.

Key Words—Bond length, Cation distribution, Chlorite, Crystal structure, Polytype, Single crystal X-ray diffraction.

INTRODUCTION

Large, light-green platelets of chlorite from Kinyiki Hill, Mtito Andei, at the edge of the Rift Valley in the Mochako District, Kenya (Harvard Museum #97703, labeled corundophillite), were found to contain intergrown triclinic *Iib*-4 and monoclinic *Iib*-2 polytypes. The chlorite platelets have been described as intergrown with corundum and pink margarite and to occur near the contact of a dike-like intrusion of dunite into hornblende schists (Parkinson, 1947). Neither the rocks nor the chlorite appear to have been studied petrologically.

The polytypes are intergrown laterally in the plane of the large platelets. In places they are separated optically by a sharp line of demarcation. In other places the monoclinic form is embayed as a result of partial conversion to the triclinic form. Where a sharp line of separation exists, the two polytypes are in an oriented intergrowth with the line of separation parallel to [010] of the monoclinic form and to [110] of the triclinic form.

The triclinic *Iib*-4 polytype is volumetrically more abundant in the Kenyan specimen, and its structure was refined by Steinfink (1958b) by film and Fourier methods in subgroup *C1*. Steinfink reported all of the octahedrally coordinated sites to have similar electron densities in two-dimensional projections; no segregation of the heavy Fe + Cr cations was therefore apparent. Bond lengths were not reported, but were calculated by Bailey (1975) from the atomic coordinates. Bailey reported the four independent tetrahedra to have similar mean T–O values between 1.67 and 1.68 Å,

but the *cis* octahedron M3 to have a mean M–O,OH value 0.015 Å larger than those of M1 and M2 in the 2:1 octahedral sheet and cation sites M4, M5, and M6 in the interlayer sheet to have different mean values of 2.047, 2.123, and 1.995 Å, respectively. Despite the limited accuracy of Steinfink's (1958b) refinement (*R* = 14%), modern refinements of the *Iib*-4 structure by Joswig *et al.* (1980) and Phillips *et al.* (1980) confirmed the tendency for Mg and Al to order within the interlayer sheet. The larger *cis* M3 site, however, is contrary to the normal ordering pattern in micas, in which the *trans* site M1 is larger.

The monoclinic *Iib*-2 polytype has been reported previously only from a waterworks tunnel excavation in Washington, D.C. (Steinfink, 1958a, 1961; Rule and Bailey, 1987) and from the Achmatov mine, Ural Mountains, U.S.S.R. (Joswig *et al.*, 1989), although its apparent rarity may be in part related to the paucity of studies of chlorites by single crystal methods. We have also found this polytype in colorless crystals from Wood's mine, Lancaster County, Pennsylvania (University of Wisconsin Museum #6002/1). Locating intergrown triclinic and monoclinic polytypes in the same platelet in the Kenyan crystals, and therefore of similar compositions and presumably subject to similar crystallization conditions, offered a unique opportunity to compare their cation-ordering patterns and to determine if structural differences exist that favor one polytype over the other. Additional refinements of chlorite structures are also desirable to determine if ordering occurs in the octahedral sites of the 2:1 layer (none found by modern refinements to date) and to assess

Table 1. Microprobe data for Kenyan chlorite.

Wt. %	I b -2	I b -4
SiO ₂	31.66 ± 0.10	31.66 ± 0.08
Al ₂ O ₃	14.38 ± 0.11	14.40 ± 0.12
MgO	32.88 ± 0.11	32.78 ± 0.11
FeO ¹	4.65 ± 0.03	4.63 ± 0.03
Cr ₂ O ₃	1.72 ± 0.04	1.68 ± 0.03
NiO	0.11	0.14
TiO ₂	0.06	0.01
K ₂ O	0.01	0.01
CaO	<0.01	<0.01
Na ₂ O	<0.01	<0.01
Cl	<0.01	<0.01
F	<0.01	0.02

¹ Converted to Fe₂O₃ and FeO by assuming the same Fe³⁺:Fe²⁺ ratio determined by Steinfink (1958b).

the validity of the predictions of Rule and Bailey (1987) as to cation ordering in chlorite (see below). The Kenyan chlorite is anomalous also in having 1.7% Cr₂O₃ and a green color rather than the usual purple color of Cr-bearing chlorite. On the basis of the optical absorption spectra reported by Neuhaus (1960), the green color indicates that the Cr is in the 2:1 octahedral sheet and that it is coordinated primarily by oxygen rather than entirely by hydroxyl groups in the interlayer sheet. A similar coordination for Cr is known in the green mica fuchsite. For ten purple, Cr-bearing chlorite samples studied by Phillips *et al.* (1980), electron density projections showed the Cr to be in the interlayer sheet. It was therefore of interest to determine if the Kenyan green chlorite is an exception to this general trend.

EXPERIMENTAL

Crystals suitable for structural refinement were found by X-ray precession study. The crystals finally selected showed no stacking disorder and no consequent streaking of $k \neq 3n$ reflections. The I**b**-4 crystal measured $0.75 \times 0.4 \times 0.01$ mm in size, and the I**b**-2 crystal measured $1.0 \times 0.5 \times 0.01$ mm in size (University of Wisconsin Museum #1784/1,2). Unit-cell parameters of $a = 5.328(1)$, $b = 9.228(2)$, $c = 14.368(4)$ Å, $\alpha = 90.46(2)^\circ$, $\beta = 97.39(2)^\circ$, and $\gamma = 89.96(2)^\circ$ for the I**b**-4 polytype and $a = 5.328(2)$, $b = 9.228(3)$, $c = 14.363(5)$ Å, and $\beta = 96.82(3)^\circ$ for the I**b**-2 polytype were determined by least-squares refinement of 14 high-angle reflections ($2\theta = 65^\circ$ to 87°). Two sets of intensity data were collected: one in the $\theta:2\theta$ variable-scan mode for the I**b**-2 structure and one in the ω -scan mode for the I**b**-4 structure. In both sets intensities were measured over all octants to $2\theta = 60^\circ$ with graphite-monochromatized MoK α radiation in a Nicolet P2₁ automated single-crystal diffractometer. Crystal and electronic stability were checked by monitoring two standard reflections after every 50 reflections. The integrated intensity (I) was calculated from $I = [S - (B1 + B2)/$

Br]Tr, where S is the scan count, B1 and B2 are the background counts, Br is the ratio of background time to scan time, and Tr is the 2θ scan rate in $^\circ/\text{min}$. Reflections were considered to be observed if $I > 3\sigma(I)$. Integrated intensities were corrected for Lp factors and for absorption by using the semi-empirical psi-scan technique of North *et al.* (1968). For the I**b**-4 polytype 4252 observed reflections were merged into 2044 independent triclinic reflections. For the I**b**-2 polytype 4271 observed reflections were merged into 1096 independent monoclinic reflections. No reflections were removed from the data sets during refinement. The sense of the Z axis for the triclinic polytype was determined by comparison of observed and calculated F values.

The composition of the Kenyan chlorite was determined as $(\text{Mg}_{4.90}\text{Al}_{0.75}\text{Fe}^{3+}_{0.17}\text{Fe}^{2+}_{0.07}\text{Cr}_{0.18})(\text{Si}_{2.60}\text{Al}_{1.40})\text{O}_{10}(\text{OH})_8$ by Steinfink (1958b) using wet chemical analysis. Bailey (1975) reported electron microprobe analyses for the same sample to give $(\text{Mg}_{4.69}\text{Al}_{0.67}\text{Fe}^{3+}_{0.26}\text{Fe}^{2+}_{0.11}\text{Cr}_{0.15}\text{Ni}_{0.01})(\text{Si}_{3.02}\text{Al}_{0.98})\text{O}_{10}(\text{OH})_8$ on the assumption of the same Fe³⁺:Fe²⁺ ratio (2.4) as found by Steinfink. New electron microprobe measurements of the present study found no significant chemical differences between the monoclinic and triclinic polytypes present in the same probe mount (Table 1), in accord with the similarity in the cell dimensions. Using the analysis for the dominant I**b**-4 polytype, the resulting formula on the basis of 28 positive charges is $(\text{Mg}_{4.715}\text{Al}_{0.694}\text{Fe}^{3+}_{0.269}\text{Fe}^{2+}_{0.109}\text{Cr}_{0.128}\text{Ni}_{0.011}\square_{0.073})(\text{Si}_{3.056}\text{Al}_{0.944})\text{O}_{10}(\text{OH})_8$, where $\square$ represents a vacancy. This formula is virtually the same as that reported by Bailey (1975) and differs from that reported by Steinfink (1958b) primarily by its tetrahedral Al content. This chlorite is a clinochlore in the preferred terminology of Bayliss (1975).

REFINEMENT

The atomic coordinates of Phillips *et al.* (1980) for the Day Book Body chlorite were used as a starting point for refinement of the triclinic I**b**-4 polytype assuming the ideal $C\bar{1}$ space group and those of Rule and Bailey (1987) for the monoclinic I**b**-2 polytype assuming the ideal $C2/m$ space group. Scattering factors from Cromer and Mann (1968) corresponding to 50% ionization were used in the refinement. Complete cation disorder was assumed at the start for the overall composition and modified according to the ordering patterns found as refinement progressed. Unit weights were found to be more appropriate than sigma weights during refinement, as is usually the case for phyllosilicates. A modified ORFLS program (Busing *et al.*, 1962) was used to refine the scale factor, atomic coordinates, isotropic B values, and then anisotropic values. After refinement ceased, bond lengths and difference-electron-density (DED) maps were used to determine any ordering of cations and to locate the positions of the

Table 2. Atomic coordinates and temperature factors of triclinic I**b**-4 and monoclinic I**b**-2 Kenyan chlorite samples.

Atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
(a) Triclinic I b -4									
M1	0.0000(0)	0.0000(0)	0.0000(0)	0.0032(5)	0.0014(2)	0.0011(1)	0.0014(2)	0.0002(2)	0.0002(1)
M2	0.0012(2)	0.3338(1)	-0.0000(1)	0.0033(3)	0.0014(1)	0.0012(1)	0.0012(2)	0.0004(1)	0.0001(1)
M3	-0.0005(2)	0.1667(1)	0.5000(1)	0.0032(4)	0.0013(1)	0.0015(1)	0.0013(2)	0.0005(1)	0.0001(1)
M4	0.0000(0)	0.5000(0)	0.5000(0)	0.0052(5)	0.0021(2)	0.0016(1)	0.0014(2)	0.0004(1)	0.0001(1)
T1	0.2328(2)	0.1692(1)	0.1922(1)	0.0053(4)	0.0021(1)	0.0015(1)	0.0015(2)	0.0004(1)	0.0002(1)
T2	0.7336(2)	0.0023(1)	0.1921(1)	0.0054(4)	0.0021(1)	0.0015(1)	0.0015(2)	0.0004(1)	0.0002(1)
OH1	0.6922(5)	0.3340(3)	0.0741(2)	0.0068(9)	0.0029(3)	0.0016(1)	0.0018(4)	0.0007(3)	0.0002(2)
OH2	0.1595(5)	-0.0012(3)	0.4299(2)	0.0107(10)	0.0031(3)	0.0014(1)	0.0012(4)	0.0004(3)	0.0001(2)
OH3	0.1339(5)	0.3406(3)	0.4298(2)	0.0094(9)	0.0037(3)	0.0014(1)	0.0011(4)	0.0004(3)	0.0001(2)
OH4	0.6336(6)	0.1565(3)	0.4305(2)	0.0093(9)	0.0037(3)	0.0014(1)	0.0022(4)	0.0005(3)	-0.0000(2)
O1	0.1936(5)	0.1673(3)	0.0771(2)	0.0059(8)	0.0026(3)	0.0015(1)	0.0016(4)	0.0004(3)	0.0002(1)
O2	0.6931(5)	0.0008(3)	0.0773(2)	0.0063(9)	0.0026(3)	0.0016(1)	0.0018(4)	0.0005(3)	0.0001(2)
O3	0.2114(6)	0.3363(6)	0.2333(2)	0.0157(11)	0.0041(4)	0.0019(1)	0.0015(5)	0.0006(3)	0.0000(2)
O4	0.5145(6)	0.1034(3)	0.2336(2)	0.0119(10)	0.0052(4)	0.0019(1)	0.0027(5)	0.0004(3)	0.0001(2)
O5	0.0152(1)	0.0687(1)	0.2335(2)	0.0126(17)	0.0051(6)	0.0019(2)	0.0009(5)	0.0002(3)	0.0002(2)
H1	0.7050	0.3330	0.1300						
H2	0.1270	0.0180	0.3680						
H3	0.1310	0.3410	0.3700						
H4	0.5950	0.1500	0.3690						
(b) Monoclinic I b -2									
M1	0.0000(0)	0.0000(0)	0.0000(0)	0.0036(8)	0.0014(3)	0.0009(1)	0.0000(0)	0.0007(2)	0.0000(0)
M2	0.0000(0)	0.3327(2)	0.0000(0)	0.0031(5)	0.0015(2)	0.0010(1)	0.0000(0)	0.0005(2)	0.0000(0)
M3	0.0000(0)	0.1665(2)	0.5000(0)	0.0020(6)	0.0013(2)	0.0011(1)	0.0000(0)	0.0004(2)	0.0000(0)
M4	0.0000(0)	0.5000(0)	0.5000(0)	0.0116(8)	0.0041(3)	0.0023(1)	0.0000(0)	0.0007(2)	0.0000(0)
T1	0.2279(2)	0.1667(1)	0.1918(1)	0.0048(3)	0.0020(1)	0.0011(1)	0.0001(2)	0.0004(1)	0.0001(1)
OH1	0.1889(9)	0.5000(0)	0.0740(3)	0.0064(14)	0.0027(5)	0.0012(2)	0.0000(0)	0.0009(4)	0.0000(0)
OH2	0.1542(10)	0.0000(0)	0.4299(3)	0.0137(17)	0.0033(5)	0.0012(2)	0.0000(0)	0.0004(5)	0.0000(0)
OH3	0.1394(6)	0.3390(4)	0.4297(2)	0.0105(11)	0.0046(4)	0.0014(1)	-0.0008(6)	0.0002(3)	-0.0002(2)
O1	0.1910(6)	0.1669(4)	0.0770(4)	0.0052(9)	0.0026(3)	0.0013(1)	0.0002(5)	0.0007(3)	-0.0001(2)
O2	0.2064(10)	0.0000(0)	0.2331(4)	0.0151(18)	0.0039(6)	0.0015(2)	0.0000(0)	0.0010(5)	0.0000(0)
O3	0.5074(7)	0.2325(4)	0.2333(2)	0.0110(11)	0.0052(4)	0.0016(2)	-0.0008(6)	0.0004(3)	0.0001(2)
H1	0.2610	0.5000	0.1280						
H2	0.1410	0.0000	0.3680						
H3	0.1710	0.2760	0.4010						

Table 3. Observed bond lengths (Å) of Kenyan chlorite.

Triclinic IIb-4					
In 2:1 layer					
To T1	O1-T1	1.641(3)	To T2	O2-T2	1.636(3)
	O3-T1	1.655(4)		O3-T2	1.657(4)
	O4-T1	1.657(3)		O4-T2	1.659(3)
	O5-T1	<u>1.656(4)</u>		O5-T2	<u>1.657(4)</u>
	Mean	1.652(2)		Mean	1.652(2)
In T1	O1-O3	2.713(5)	In T2	O2-O3	2.709(5)
	O1-O4	2.712(4)		O2-O4	2.712(5)
	O1-O5	2.714(5)		O2-O5	2.713(5)
	O3-O4	2.685(5)		O3-O4	2.678(5)
	O3-O5	2.683(5)		O3-O5	2.689(5)
	O4-O5	<u>2.678(5)</u>		O4-O5	<u>2.684(5)</u>
	Mean	2.698(2)		Mean	2.698(2)
To M1	O1-M1	2.087(3) × 2	To M2	O1-M2	2.081(3)
	O2-M1	2.090(3) × 2		O2-M2	2.089(3)
	OH1-M1	<u>2.066(3)</u> × 2		OH1-M2	2.071(4)
	Mean	2.081(2)		O1-M2	2.090(3)
In M1 shared	O1-O2	2.825(4) × 2		O2-M2	2.083(3)
	OH1-OH1	2.791(4) × 2		OH1-M2	<u>2.071(3)</u>
	O2-OH1	<u>2.798(4)</u> × 2		Mean	2.081(1)
	Mean	2.805(2)	In M2 shared	O1-O1	2.830(6)
				O1-OH1	2.791(4)
In M1 unshared	O1-O2	3.078(5) × 2		O2-O1	2.825(4)
	O1-OH1	3.076(5) × 2		O2-O2	2.827(6)
	O2-OH1	<u>3.074(4)</u> × 2		OH1-O2	2.798(4)
	Mean	3.076(3)		OH1-OH1	<u>2.755(6)</u>
In interlayer				Mean	2.804(2)
	To M3		In M2 unshared	O1-O2	3.069(4)
	OH2-M3	2.081(3)		O1-OH1	3.076(5)
	OH2-M3	2.077(4)		O2-OH1	3.076(5)
	OH3-M3	2.080(4)		O1-O2	3.078(5)
In M3 shared	OH3-M3	2.079(3)		O1-OH1	3.074(4)
	OH4-M3	2.074(3)		O2-OH1	<u>3.076(5)</u>
	OH4-M3	<u>2.078(3)</u>		Mean	3.075(2)
	Mean	2.078(1)	To M4	OH2-M4	1.957(3) × 2
	OH2-OH2	2.797(6)		OH3-M4	1.962(3) × 2
	OH2-OH3	2.619(4)		OH4-M4	<u>1.949(3)</u> × 2
	OH3-OH3	2.794(6)		Mean	1.956(2)
	OH3-OH4	2.607(4)	In M4 shared	OH2-OH3	2.619(4) × 2
In M3 unshared	OH4-OH4	2.797(7)		OH2-OH4	2.601(4) × 2
	OH4-OH2	<u>2.601(4)</u>		OH3-OH4	<u>2.607(4)</u> × 2
	Mean	2.703(2)		Mean	2.609(2)
	OH2-OH3	3.157(5)	In M4 unshared	OH2-OH3	2.915(4) × 2
	OH2-OH4	3.154(5)		OH2-OH4	2.915(5) × 2
	OH2-OH3	3.159(5)		OH3-OH4	<u>2.915(5)</u> × 2
	OH2-OH4	3.163(5)		Mean	2.915(3)
	OH3-OH4	3.163(5)			
	OH3-OH4	<u>3.154(5)</u>			
	Mean	3.158(2)			
				OH1-H1	0.80
				OH2-H2	0.90
				OH3-H3	0.86

Table 3. Continued.

			OH4-H4	0.88	
			Mean	0.860	
H-bonds	OH2-O5	2.906(5)	OH2-H2-O5	173°	
	OH3-O3	2.906(5)	OH3-H3-O3	167°	
	OH4-O4	<u>2.857(5)</u>	OH4-H4-O4	171°	
	Mean	2.890(3)			
Monoclinic <i>I1b</i> -2					
In 2:1 layer					
To T1	O1-T1	1.637(3)	In T1	O1-O2	2.713(5)
	O2-T1	1.658(2)		O1-O3	2.711(5)
	O3-T1	1.653(4)		O1-O3	2.717(5)
	O3-T1	<u>1.663(4)</u>		O2-O3	2.687(5)
	Mean	1.653(2)		O2-O3	2.678(5)
			O3-O3	<u>2.684(1)</u>	
			Mean	2.698(2)	
To M1	OH1-M1	2.073(5) × 2	To M2	OH1-M2	2.067(4) × 2
	O1-M1	<u>2.089(3)</u> × 4		O1-M2	2.081(4) × 2
	Mean	2.084(2)		O1-M2	<u>2.090(3)</u> × 2
			Mean	2.079(2)	
In M1 shared	OH1-O1	2.796(5) × 4	In M2 shared	OH1-OH1	2.749(10)
	O1-O1	<u>2.822(6)</u> × 2		O1-O1	2.822(6)
	Mean	2.805(3)		OH1-O1	2.796(5) × 2
			O1-O1	<u>2.823(6)</u> × 2	
			Mean	2.802(3)	
In M1 unshared	OH1-O1	3.083(6) × 4	In M2 unshared	O1-OH1	3.074(4) × 2
	O1-O1	<u>3.080(7)</u> × 2		O1-O1	3.074(4) × 2
	Mean	3.082(4)		O1-OH1	<u>3.074(6)</u> × 2
			Mean	3.074(3)	
In interlayer					
To M3	OH2-M3	2.061(4) × 2	To M4	OH2-M4	1.992(5) × 2
	OH3-M3	2.070(4) × 2		OH3-M4	<u>1.989(4)</u> × 4
	OH3-M3	<u>2.062(3)</u> × 2		Mean	1.990(3)
	Mean	2.064(2)			
In M3 shared	OH2-OH2	2.746(10)	In M4 shared	OH2-OH3	2.638(5) × 4
	OH3-OH3	2.645(7)		OH3-OH3	<u>2.645(7)</u> × 2
	OH2-OH3	2.638(5) × 2		Mean	2.640(3)
	OH2-OH3	<u>2.757(5)</u> × 2			
	Mean	2.697(5)			
In M3 unshared	OH2-OH3	3.129(6) × 2	In M4 unshared	OH2-OH3	2.982(6) × 4
	OH2-OH3	3.119(4) × 2		OH3-OH3	<u>2.971(8)</u> × 2
	OH3-OH3	<u>3.130(4)</u> × 2		Mean	2.978(4)
	Mean	3.126(3)			
	OH1-H1	0.82			
	OH2-H2	0.88			
	OH3-H3	<u>0.74</u> × 2			
	Mean	0.80			
H-bonds	OH2-O2	2.873(5)			
	OH3-O3	<u>2.901(5)</u> × 2			
	Mean	2.892(3)			

H⁺ protons associated with the OH groups. Final refinements with revised scattering factor tables and incorporating (but not varying) the H⁺ positions reduced the residuals to R = 4.2% for the triclinic *I1b*-4 polytype as *C* $\bar{1}$ and R = 5.9% for the monoclinic *I1b*-2 polytype as *C*2/*m*. DED maps were flat at all atomic positions at this point. Observed and calculated structure am-

plitudes may be obtained from the authors upon request. Atomic coordinates and thermal parameters are listed in Table 2, bond lengths and angles in Table 3, and orientations of the thermal ellipsoids in Table 4.

The final residual values of 4 to 6% are reasonable for the quality of the crystals used, but sufficiently high that ordering in subgroup symmetry was examined for

Table 4. Orientations of thermal ellipsoids of Kenyan chlorite.

Atom	Axis	RMS displacement (Å)	Angles (°) with respect to		
			X	Y	Z
IIb-4					
M1	R1	0.043(8)	39(5)	128(5)	87(4)
	R2	0.094(4)	51(5)	41(7)	104(14)
	R3	0.107(4)	89(10)	103(12)	165(14)
M2	R1	0.048(5)	38(4)	128(4)	92(3)
	R2	0.092(3)	52(4)	39(4)	105(7)
	R3	0.109(3)	93(5)	100(6)	165(7)
M3	R1	0.042(6)	39(4)	129(4)	93(2)
	R2	0.091(3)	51(4)	39(4)	98(4)
	R3	0.123(3)	90(3)	93(3)	172(3)
M4	R1	0.068(5)	39(5)	128(5)	92(3)
	R2	0.108(4)	51(5)	39(5)	100(7)
	R3	0.127(3)	90(5)	96(6)	170(7)
T1	R1	0.067(4)	40(3)	129(3)	89(2)
	R2	0.109(3)	50(3)	40(4)	102(8)
	R3	0.124(3)	90(5)	99(6)	168(8)
T2	R1	0.068(4)	40(3)	130(3)	90(2)
	R2	0.109(3)	50(3)	41(4)	103(7)
	R3	0.125(3)	91(5)	100(6)	167(7)
OH1	R1	0.078(8)	34(7)	124(7)	95(6)
	R2	0.120(6)	121(8)	138(11)	60(18)
	R3	0.135(6)	103(10)	111(14)	150(18)
OH2	R1	0.104(7)	54(11)	143(11)	87(16)
	R2	0.122(6)	91(28)	82(23)	11(31)
	R3	0.131(6)	144(11)	126(12)	80(32)
OH3	R1	0.106(6)	33(12)	121(11)	85(15)
	R2	0.124(6)	104(24)	92(34)	7(29)
	R3	0.131(6)	120(15)	149(11)	95(38)
OH4	R1	0.092(7)	38(6)	128(6)	95(9)
	R2	0.125(6)	90(12)	90(14)	7(13)
	R3	0.141(6)	128(6)	142(6)	85(17)
O1	R1	0.075(8)	35(7)	125(7)	90(6)
	R2	0.117(6)	55(9)	41(20)	114(39)
	R3	0.123(6)	97(23)	109(32)	156(39)
O2	R1	0.074(8)	38(7)	127(6)	92(6)
	R2	0.120(6)	53(8)	40(12)	110(27)
	R3	0.130(6)	97(17)	104(22)	159(27)
O3	R1	0.124(6)	61(8)	150(9)	91(17)
	R2	0.139(6)	86(16)	86(17)	12(16)
	R3	0.156(6)	150(9)	119(8)	78(16)
O4	R1	0.111(7)	35(5)	124(5)	88(9)
	R2	0.141(6)	97(10)	86(10)	5(10)
	R3	0.164(6)	124(5)	146(5)	86(11)
O5	R1	0.124(6)	144(14)	68(11)	110(15)
	R2	0.142(6)	117(24)	86(42)	20(17)
	R3	0.147(6)	112(24)	157(14)	93(43)
IIb-2					
M1	R1	0.065(9)	116(9)	90(0)	113(9)
	R2	0.077(8)	90(0)	0(0)	90(0)
	R3	0.101(6)	106(9)	90(0)	157(9)
M2	R1	0.064(6)	173(6)	90(0)	76(6)
	R2	0.081(5)	90(0)	0(0)	90(0)
	R3	0.102(4)	97(6)	90(0)	166(6)
M3	R1	0.052(8)	180(4)	90(0)	83(4)
	R2	0.074(6)	90(0)	0(0)	90(0)
	R3	0.106(4)	90(4)	90(0)	173(4)
M4	R1	0.128(4)	180(2)	90(1)	83(8)
	R2	0.134(4)	90(1)	0(1)	90(0)
	R3	0.153(4)	90(8)	90(0)	173(8)

Table 4. Continued.

Atom	Axis	RMS displacement (Å)	Angles (°) with respect to		
			X	Y	Z
T1	R1	0.082(3)	177(9)	87(14)	81(5)
	R2	0.092(3)	88(15)	14(8)	104(8)
	R3	0.109(3)	93(4)	104(7)	163(7)
OH1	R1	0.088(11)	25(17)	90(0)	122(17)
	R2	0.108(10)	90(0)	0(0)	90(0)
	R3	0.114(9)	115(17)	90(0)	148(17)
OH2	R1	0.111(10)	90(14)	90(0)	173(14)
	R2	0.120(9)	90(0)	0(0)	90(0)
	R3	0.140(9)	180(13)	90(0)	83(14)
OH3	R1	0.115(7)	125(33)	102(14)	135(36)
	R2	0.123(6)	138(33)	104(16)	45(36)
	R3	0.143(6)	70(13)	160(13)	92(13)
O1	R1	0.083(8)	168(12)	82(15)	74(9)
	R2	0.106(7)	82(16)	12(32)	83(37)
	R3	0.115(6)	98(11)	80(38)	162(18)
O2	R1	0.123(9)	72(17)	90(0)	169(17)
	R2	0.131(9)	90(0)	0(0)	90(0)
	R3	0.147(9)	162(17)	90(0)	101(17)
O3	R1	0.123(6)	163(12)	106(13)	89(46)
	R2	0.129(6)	93(45)	101(17)	11(13)
	R3	0.153(6)	73(7)	161(10)	101(12)

both crystals. Bond lengths in the ideal space groups indicated disorder of the tetrahedral Si,Al cations (Table 3), in accord with the finding of Phillips *et al.* (1980) and Rule and Bailey (1987) that little or no driving force exists in the *Ib* structure to favor localization of Al in any of the tetrahedral sites. Major interest thus focused on ordering of octahedrally coordinated cations in subgroups C1 for *Ib*-4 and C2 or *Cm* for *Ib*-2. Atomic coordinates for ordered models in these subgroups involving both tetrahedral and octahedral cations were determined from the distance-least-squares program OPTDIS of Dollase (1980), and then refined by ORFLS. One atom was held constant in all refinements in these noncentrosymmetric subgroups. The atomic coordinates of all cations refined to their positions within the ideal space groups. Thus, the ideal space groups appear to be correct for both specimens. These space groups are both in accord with the observation by Guggenheim *et al.* (1983) that this sample did not produce a positive optical second harmonic generation response, suggesting, but not proving, that the sample is centrosymmetric.

DISCUSSION

Disorder of tetrahedral cations

The independent tetrahedra T1 and T2 in the triclinic *Ib*-4 polytype from Kenya are identical in size (mean T-O = 1.652 Å, Table 3) in the ideal space group *C1*, and ordered models with four independent tetrahedra in subgroup C1 refined to the disordered positions. Only one independent tetrahedron exists in the ideal space group *C2/m* of the monoclinic *Ib*-2 polytype (mean T-O = 1.653 Å), and ordered models containing

two independent tetrahedra in subgroups *C2* and *Cm* refined to disordered positions. The ordered model in subgroup *Cm* is unreasonable also in that it requires the two tetrahedral sheets in the same 2:1 layer to be of different compositions. Thus, both structures are disordered and agree in this respect with all other *Iib* structures refined by modern methods.

The observed mean values of 1.652 and 1.653 Å for an Al^{IV} content of 0.944 atoms per formula unit compare favorably with mean T–O values for similar tetrahedral compositions of chlorites found by other workers (e.g., 1.652 and 1.654 Å for $\text{Al}^{\text{IV}} = 0.98$ by Phillips *et al.*, 1980; 1.651 and 1.650 Å for $\text{Al}^{\text{IV}} = 0.84$ by Joswig *et al.*, 1980; 1.650 and 1.652 Å for $\text{Al}^{\text{IV}} = 1.00$ by Bailey, 1986; 1.656 and 1.661 Å for $\text{Al}^{\text{IV}} = 1.01$ by Phillips *et al.*, 1980). They are not in accord with the higher Al^{IV} value of 1.4 reported by Steinfink (1958b) for the same specimen. According to the results of Rule and Bailey (1987), a tetrahedral Al content of 1.4 corresponds to a mean T–O bond length of 1.668 Å.

The thermal ellipsoids of the basal oxygens (Table 4) are oriented so that the direction of maximum vibration is normal to the T–O_b bonds in both structures.

Ordering of octahedral cations

Sites M1 and M2 in the 2:1 octahedral sheet are similar to one another in size in both structures in the ideal space groups, within experimental error, and the two *cis* octahedral cations did not refine to different positions on uncoupling via ordered models in subgroup symmetries. Thus, these cations are disordered also. The larger size of one *cis* octahedron in the Kenyan *Iib*-4 structure of Steinfink (1958b) is therefore an artifact due to limited data and incomplete refinement.

The Cr could not be located unequivocally, except that it is in octahedral rather than tetrahedral coordination, due to the presence of a larger amount of Fe^{3+} . Initial refinement cycles indicated cation disorder over the M1 and M2 octahedral sites of the 2:1 layer for both structures, but cation ordering over the M3 and M4 interlayer sites, with about twice as many heavy atoms in the interlayer sheet as in the 2:1 layer. Because of the green color of the platelets, Cr was assigned to the octahedral sheet of the 2:1 layer, assuming disorder along with Fe^{3+} and Mg over sites M1 and M2. At no stage of the refinement did DED maps indicate any segregation of heavy and light atoms over sites M1 and M2. The composition that gives the best fit between

observed and calculated values of bond lengths and electron densities for M1 and M2 is $(\text{Mg}_{0.905}\text{Cr}_{0.043}\text{Fe}^{3+}_{0.052})^{0.095+}$. A mean M–O,OH bond length calculated for this composition using the ionic radii of Shannon (1976) is 2.082 Å, and an electron density calculated assuming 50% ionization is 12.2 e[−]. These values compare favorably with observed mean bond lengths of $\text{M1} = \text{M2} = 2.082$ Å for *Iib*-4 and $\text{M1} = 2.084$ and $\text{M2} = 2.079$ Å for *Iib*-2 and an observed electron density of 11.5 e[−] for both sites in both structures. DED maps calculated on the basis of a random distribution of the composition shown above showed flat residuals for both the M1 and M2 sites. No significance is attached to the slightly different sizes of M1 and M2 in the *Iib*-2 structure, and the 2:1 layer is considered identical in the two polytypes.

The main interest in the structures concerns the ordering of the cations of the interlayer sheet. The smaller trivalent Al and Fe cations proved to be concentrated in site M4 located on a center of symmetry. This is the same ordering pattern found in all other structurally refined trioctahedral chlorites, although the degree of ordering has been found to vary from specimen to specimen. Surprisingly, the degree of ordering differs in these intergrown polytypes as well. The mean M–O,OH bond lengths for M3 and M4 are 2.079 and 1.957 Å, respectively, for the triclinic *Iib*-4 polytype, but are 2.064 and 1.990 Å for the monoclinic *Iib*-2 polytype (Table 3). These are significant differences considering the errors involved. The compositions for the sites that give the best fit between observed and calculated bond lengths and electron densities are shown in Table 5.

The ionic radius of a vacancy was taken as 0.82 Å from the data of Weiss *et al.* (1985). These best-fit compositions when combined with those of the 2:1 layer agree exactly with the overall composition as determined from Table 1.

The two structures thus differ only in the distribution of Mg and Al over sites M3 and M4 of the interlayer sheet. The monoclinic *Iib*-2 structure is less ordered in its interlayer sheet than the triclinic *Iib*-4 structure, despite the fact that the overall compositions are similar and that they occur immediately adjacent to one another in the platelets. The low degree of ordering is not dictated by the monoclinic structure itself, because a *Iib*-2 polytype from a different locality was found by Rule and Bailey (1987) to be completely ordered, with only Al in that site (mean M4–O,OH = 1.929 Å). The

Table 5. Compositions of best fits between observed and calculated bond lengths and electron densities.

Polytype		Compositions	M–O,OH		(Å)		Electron density (e [−])	
			Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
<i>Iib</i> -4	M3 × 2	(Mg _{1.0}) ⁰	2.079	2.070	11.0	11.0		
	M4 × 1	(Al _{0.694} Fe ³⁺ _{0.113} Fe ²⁺ _{0.109} Ni _{0.011} □ _{0.073}) ^{0.661+}	1.957	1.947	13.8	12.8		
<i>Iib</i> -2	M3 × 2	(Mg _{0.90} Al _{0.10}) ^{0.10+}	2.064	2.052	11.0	11.05		
	M4 × 1	(Mg _{0.20} Al _{0.494} Fe ³⁺ _{0.113} Fe ²⁺ _{0.109} Ni _{0.011} □ _{0.073}) ^{0.461+}	1.990	1.983	15.0	13.7		

Table 6. Other important structural features of Kenyan chlorite.

Parameter	Sites	I b -4	I b -2
Octahedral distortion RMS (15)	M1	4.74	4.82
	M2	4.76	4.81
	M3	8.45	7.76
	M4	5.66	6.18
Octahedral distortion RMS (36)	M1	3.28	3.33
	M2	3.29	3.33
	M3	5.99	5.52
	M4	3.96	4.35
Octahedral rotation (°)	M1	0.00	0.00
	M2	0.04	0.09
	M3	5.03	3.10
	M4	0.00	0.00
Octahedral flattening Ψ_{oct} (°)	M1	58.6	58.7
	M2	58.6	58.6
	M3	61.3	61.0
	M4	59.3	59.8
Tetrahedral angle τ_{tet} (°)	T1	110.8	110.9
	T2	110.8	
Tetrahedral rotation α_{tet} (°)		6.9	6.8
Sheet thickness (Å)			
Tetrahedral		2.241	2.242
2:1 octahedral		2.171	2.168
Interlayer		1.994	2.005
Interlayer separation (Å)			
β_{ideal} (°)		2.802	2.803
Avg. M3-T distances (Å)		97.1	97.1
Avg. M4-T distances (Å)		4.720	4.727
		4.739	4.748

monoclinic form is apparently in the process of being converted isochemically to the triclinic form. The textural relations and the structural refinement suggest that the monoclinic form is less stable than the triclinic form, in accord with the much greater abundance in nature of the triclinic form. Rule and Bailey (1987) noted that the triclinic I**b**-4 structure should be twice as abundant as the monoclinic I**b**-2 structure if only the geometry of layer superpositions is considered, and that other factors must also be important to account for the observed lesser abundance of the monoclinic form. The Kenyan specimens suggest that the other factors relate to the inherent energetics of the two structures rather than to different environments of crystallization.

Layer offsets

For the two triclinic I**b**-4 structures they refined, Phillips *et al.* (1980) noted that cation-cation repulsion between the trivalent cation in M4 and the tetrahedral cations in the sheets immediately above and below the interlayer sheet offsets the two adjacent tetrahedral sheets in opposite directions. The offsets are diagonal to the *X* and *Y* axes along [110]; hence, the crystallographic β angles for the two specimens are 0.24° and 0.42° larger than their ideal values near 97.1°, and the crystallographic α angles are 90.45° and 90.53° instead

of 90°. Phillips *et al.* (1980) cited the possibility of moving the cations apart in this manner as one reason for the ordering of a trivalent cation into site M4. This effect is not possible with a trivalent cation in M3. A similar offset of the tetrahedral sheets was found in the monoclinic I**b**-2 structure by Rule and Bailey (1987), but the direction of offset was different because of the different position of the repeating 2:1 layer (position 2 vs. position 4). The offset was found parallel to [100] rather than [110], and only the crystallographic β angle was affected as a result, decreasing to 96.35° from its ideal value of 97.18°.

Similar offsets of the tetrahedral sheets occur in the two structures of the present study, but the magnitudes are determined by the degree of ordering of the interlayer cations. For the triclinic I**b**-4 polytype the magnitudes of the offsets and the resulting values of the crystallographic angles are close to those found by Phillips *et al.* (1980). The shift of adjacent surfaces of 2:1 layers, which are constrained in position by relatively weak hydrogen bonds to the intercalated interlayer sheet, is ideally +0.333 a_3 relative to hexagonal axes. But the shift in the present study is changed by the offsets to +0.360 a_3 vs. +0.357 a_3 for the two structures of Phillips *et al.* (1980). This layer offset when combined with an intralayer shift of +0.360 a_2 produces an overall shift of repeating layers along the resultant *X* and *Y* axes of -0.347 a_1 - 0.013 b_1 (ideally only -0.333 a_1) in this study vs. -0.348 a_1 - 0.014 b_1 and -0.345 a_1 - 0.012 b_1 for the two structures of Phillips *et al.* (1980). For the monoclinic I**b**-2 polytype of this study, however, the smaller concentration of a trivalent cation in M4 leads to a smaller shift of the surfaces of adjacent layers of +0.347 a_1 and a resultant shift of repeating layers of -0.320 a_1 . The corresponding values for the I**b**-2 structure of Rule and Bailey (1987) that has complete ordering are +0.370 a_1 and -0.295 a_1 .

Tetrahedral rotation

Tetrahedral rotation angles (α) of 5.0° to 8.5° to relieve the lateral misfit of tetrahedral and octahedral sheets have been found for the eight trioctahedral chlorite samples refined to date. The two Kenyan specimens have α values of 6.9° and 6.8°. The equality of the two rotation angles in the Kenyan polytypes is another indication of their similarity in composition. In all chlorites the direction of rotation moves the basal oxygens towards the OH donors in the interlayer sheet.

Hydrogen bonding system

Joswig *et al.* (1980) accurately located the H⁺ protons of the OH groups for the I**b**-4 polytype by neutron diffraction and, on the basis of that distribution, predicted the tilting modes of the OH dipoles for Ia, Ib, and IIa structural units. The H⁺ protons were located on DED maps in the present study as regions of small

excess density, about 0.8 to 0.9 Å from the centers of their associated OH groups (Table 3). In all samples the O..H vectors of the interlayer hydroxyls are tilted slightly away from the vertical towards their basal oxygen acceptors to form bent hydrogen bonds. The O—OH distances range from 2.87 to 2.91 Å.

The probability of locating H⁺ positions accurately by X-ray diffraction in minerals of relatively poor crystallinity, such as the chlorites, is not high. For example, for the two I**b**-4 chlorites refined structurally by Phillips *et al.* (1980), the H⁺ coordinates determined by X-ray diffraction for the Day Book Body specimen agree reasonably well with those found more accurately by Joswig *et al.* (1980) by neutron diffraction. The deviations amount to 0.06 to 0.08 Å along the three axes. The coordinates for the H⁺ protons for the Siskiyou County specimen do not agree as well and must be considered largely artifacts of the DED maps. In the present study the position of H2 for the I**b**-2 polytype is reasonably close to the position predicted by neutron diffraction, but those of H1 and H3 do not agree well with the predictions. For the I**b**-4 polytype the positions of the four H⁺ positions can be described as reasonably close to those of Joswig *et al.* (1980), but with deviations that average 0.05 Å along *X*, 0.07 Å along *Y*, and 0.10 Å along *Z*.

ACKNOWLEDGMENTS

This research was supported in part by NSF grant EAR-8614868 and in part by Petroleum Research Fund grant 17966-AC2-C, administered by the American Chemical Society. The specimens used were kindly provided by C. Frondel from the Harvard Museum collection. E. D. Glover supervised the electron microprobe analyses. W. Joswig kindly provided a copy of his manuscript on I**b**-2 chlorite prior to publication.

REFERENCES

- Bailey, S. W. (1975) Chlorites: in *Soil Components*, Vol. 2, J. E. Gieseking, ed., Springer-Verlag, New York, 191–263.
- Bailey, S. W. (1986) Re-evaluation of ordering and local charge balance in 1a chlorite: *Can. Mineral.* **24**, 649–654.
- Bayliss, P. (1975) Nomenclature of the trioctahedral chlorites: *Can. Mineral.* **13**, 178–180.
- Busing, W. R., Martin, K. O., and Levy, H. A. (1962) ORFLS, a FORTRAN crystallographic least-squares refinement program: *U.S. Natl. Tech. Inf. Serv. ORNL-TM-305*.
- Cromer, D. T. and Mann, J. B. (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions: *Acta Crystallogr.* **A24**, 321–324.
- Dollase, W. A. (1980) Optimum distance model of relaxation around substitutional defects: *Phys. Chem. Minerals* **6**, 255–304.
- Guggenheim, S., Schulze, W. A., Harris, G. A., and Lin, J.-C. (1983) Noncentric layer silicates: An optical second harmonic generation, chemical, and X-ray study: *Clays & Clay Minerals* **31**, 251–260.
- Joswig, W. and Fuess, H. (1989) Neutron diffraction study of a one-layer monoclinic chlorite: *Clays & Clay Minerals* **37** (in press).
- Joswig, W., Fuess, H., Rothbauer, R., Takéuchi, Y., and Mason, S. A. (1980) A neutron diffraction study of a one-layer triclinic chlorite (penninite): *Amer. Mineral.* **65**, 349–352.
- Neuhaus, A. (1960) Über die Ionenfarben der Kristalle und Minerale am Beispiel der Chromfärbungen: *Z. Kristallogr.* **113**, 195–233.
- North, A. C. T., Phillips, D. C., and Mathews, F. S. (1968) A semi-empirical method of absorption correction: *Acta Crystallogr.* **A24**, 351–359.
- Parkinson, J. (1947) Outlines of the geology of the Mito Andei-Tsavo area, Kenya Colony: *Geol. Survey Kenya Rep.* **13**, 40 pp.
- Phillips, T. L., Loveless, J. K., and Bailey, S. W. (1980) Cr³⁺ coordination in chlorites: A structural study of ten chromian chlorites: *Amer. Mineral.* **65**, 112–122.
- Rule, A. C. and Bailey, S. W. (1987) Refinement of the crystal structure of a monoclinic ferroan clinocllore: *Clays & Clay Minerals* **35**, 129–138.
- Shannon, R. D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides: *Acta Crystallogr.* **A32**, 751–767.
- Steinfink, H. (1958a) The crystal structure of chlorite. I. A monoclinic polymorph: *Acta Crystallogr.* **11**, 191–195.
- Steinfink, H. (1958b) The crystal structure of chlorite. II. A triclinic polymorph: *Acta Crystallogr.* **11**, 195–198.
- Steinfink, H. (1961) Accuracy in structure analysis of layer silicates: Some further comments on the structure of prochlorite: *Acta Crystallogr.* **14**, 198–199.
- Weiss, Z., Rieder, M., Chmielova, M., and Krajicek, J. (1985) Geometry of the octahedral coordination in micas: A review of refined structures: *Amer. Mineral.* **70**, 747–757.

(Received 21 June 1988; accepted 1 December 1988; Ms. 1799)