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Cr^{3+} coordination in chlorites: a structural study of ten chromian chlorites

T. L. PHILLIPS, JANET K. LOVELESS AND S. W. BAILEY

Department of Geology and Geophysics
University of Wisconsin-Madison
Madison, Wisconsin 53706

Abstract

In an effort to provide additional information on the coordination of Cr^{3+} in chlorites, complete structural refinements were undertaken of two chromian chlorites from Day Book Body, North Carolina, and Siskiyou Co., California, both of which have been reported to contain predominantly tetrahedral Cr^{3+}. In addition, eight one-dimensional electron density projections were constructed from X-ray intensity data taken from eight different chromian chlorites, three of which were reported to have tetrahedral Cr^{3+}. The one-dimensional projections indicate the Cr^{3+} and other heavy atoms to be concentrated in the interlayer octahedral sites. There is good agreement between the number of electrons per formula unit derived from integration of cation electron density peaks and the number calculated from the microprobe analyses under the assumption that all heavy atoms are concentrated in the interlayer. Both three-dimensional studies were done on II*b*-4 polytypes in triclinic space group $C\bar{1}$. In both structures the Cr^{3+} was preferentially concentrated in the M(4) octahedron on the inversion center within the interlayer. Si and Al were found to be disordered over the two independent tetrahedra. We propose that a combination of cation repulsion and crystal field effects concentrates the Cr^{3+} in the M(4) octahedron, and that a disordered Si,Al distribution in tetrahedral sites provides the most favorable balance of charge around M(4). The cell angle α was found to be triclinic, and it is postulated that repulsion between the tetrahedral and M(4) cations causes this slewing of the structure. As no evidence of Cr^{3+} in tetrahedral coordination was found, we propose that the names kotschubeite and kämmererite be discarded.

Introduction and nomenclature

Chromium-bearing chlorites long have been of considerable mineralogical interest because of their pleasing pink to red to violet colors. There has been lack of agreement as to the structural location of the chromium, however, and as to the most appropriate species or variety names.

Lapham (1958) in the first detailed investigation of chromian chlorites studied the variations in optical, chemical, X-ray, and thermal properties of eight chromium-bearing chlorites in relation to the amount of chromium present. He found that for chlorites containing less than 2% Cr_2O_3 there was no significant change in the properties, and suggested that the prefix "Cr" be added to the accepted Fe–Mg nomenclature. In chlorites having more than 2% Cr_2O_3, however, Lapham observed significant variations in the analyzed properties, reportedly depending on whether the Cr^{3+} was tetrahedrally or octahedrally coordinated. Coordination was determined by plots of *d* spacings of certain reflections against percent Cr_2O_3. On the basis of his results, Lapham proposed that the name kämmererite be used for chromian chlorites with octahedral Cr^{3+} and that kotschubeite be used when the Cr^{3+} coordination was tetrahedral.

McCormick (1975) described a chlorite containing both octahedral and tetrahedral chromium, where coordination was determined by differing dissolution rates during acid leaching. He proposed that Lapham's classification be revised so that kämmererite include chlorites with $Cr^{VI} \geq Cr^{IV}$, and kotschubeite include chlorites with $Cr^{VI} < Cr^{IV}$. Using this nomenclature McCormick classified his specimen as kotschubeite.

Damodaran and Somasekar (1976) studied a "kämmererite" from the Nuggihalli Schist Belt, India, using Lapham's determinative methods. Their results indicated the Cr^{3+} to be tetrahedrally coordinated, and therefore the specimen to be kotschubeite instead of kämmererite.

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Besnus *et al.* (1976) postulated the presence of hexavalent Cr^{6+} in tetrahedral coordination in a pinkish-violet chlorite from Campo-Formoso, Brazil, primarily on the basis of ESCA spectra. This finding is stated by Professor R. Wey, in whose laboratory the spectra were recorded, to be the result of an incorrect interpretation of the ESCA spectra by the authors (personal communication, 1975). In addition, wet-chemical analysis and Mössbauer spectra both indicate Fe^{2+} to be present in this sample, and the presence of such a highly oxidized ion as Cr^{6+} is unlikely in close association with Fe^{2+}.

Crystal field theory suggests that Cr^{3+} has a large preference for octahedral coordination (Burns, 1970, p. 12). In fact, Burns and Burns (1975) could find no well-documented examples of Cr^{3+} in tetrahedral coordination among Cr-bearing minerals. Neuhaus (1960) gives optical absorption spectra for chromian chlorite from which a crystal field splitting energy of 63 kcal can be calculated (Burns, 1970). Neuhaus (1960) concludes further that the red-purple color of chromian chlorite can only occur if the Cr^{3+} is in the interlayer octahedral sheet. If the Cr^{3+} were in the 2:1 octahedral sheet, the color should be green as in fuchsite. Of the three X-ray structural studies done to date on Cr-rich chlorites, none have had tetrahedral Cr^{3+}; instead chromium is preferentially concentrated in the interlayer octahedral sheet[1] (Steinfink, 1958; Brown and Bailey, 1963; Lister and Bailey, 1967).

In the most diagnostic study to date, Bish (1977) examined ten chromian chlorites, including McCormick's specimen and several of Lapham's specimens, using X-ray and optical spectrographic methods to determine the coordination of Cr^{3+}. Absorption spectra gave no indication of tetrahedral coordination but were entirely consistent with octahedral coordination of Cr^{3+}. Application of X-ray determinative curves to the $00l$ reflections indicated that most of the heavy atoms were in the interlayer sheet for his specimens. As suggested by Bayliss (1975), Bish proposed that the names kotschubeite and kämmererite be dropped and that the prefixes "Cr" or "chromian" be attached to the appropriate chlorite species name.

In an effort to provide additional information on Cr^{3+} coordination in chlorites, we undertook a complete three-dimensional structural refinement of two chlorites, both previously classified as kotschubeites. In addition, we studied eight chromium-bearing chlorites, three of which have been classified as kotschubeites, with one-dimensional Fourier techniques to determine the sheet in which the Cr^{3+} is concentrated.

One-dimensional electron density projections

Precession photographs were taken of eight chromian chlorites from different localities, and the crystals exhibiting the sharpest $00l$ reflections were selected for further study. All crystals, except those of the San Benito specimen, showed streaking of $k \neq 3n$ reflections. However, as only $00l$ data were to be collected, this did not pose a problem. Microprobe analysis was done on all crystals, and structural formulas based on 28 positive charges were computed for each sample. The results are shown in Table 1. Each crystal was mounted on a Syntex $P2_1$ automated diffractometer, and unit-cell parameters were determined using least-squares refinement of medium-angle reflections. The Nuggihalli specimen is of interest as it shows a three-layer periodicity in the $h0l$ reflections and has a c repeat of 43A with α, β, γ all roughly equal to 90°. All the other specimens have a 1-layer monoclinic-shaped unit cell with $\beta \cong 97°$. Since regular stacking is not present, the true cell symmetry cannot be determined.

The intensities of $00l$ and $00\bar{l}$ reflections were recorded to $2\theta = 96°$ in a variable scan mode with an automated single-crystal diffractometer using graphite-monochromatized Mo$K\alpha$ radiation. Only reflections for which $I > 2\sigma(I)$ were considered observed, and one reflection was monitored every ten reflections to check for crystal and electronic stability. Absorption corrections were made empirically by comparing $00l$ intensities to complete Ψ scans (10° increments in ϕ) for selected reflections at 2θ intervals of 10°. $00l$ and $00\bar{l}$ were averaged after Lorentz-polarization corrections were made. The results were used to construct a one-dimensional electron density projection at 3° intervals for each crystal. The projection for the Lancaster County, Pennsylvania, specimen is illustrated in Figure 1 as a representative example. The z/c coordinates, temperature factors, and cation multiplicities were varied by least-squares refinement to give a final residual of 7.4% for this specimen. Calculated structure factors were used to scale and assign phases to the observed data.

Examination of the electron density projection for each crystal indicated the scattering power of the interlayer octahedral sheet to be appreciably greater

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[1] Inferred, in the case of the Steinfink structure, from bond lengths calculated by the present authors from his coordinates and from a 1-dimensional electron density projection for a crystal from the same locality.

Table 1. Electron microprobe analyses of ten chromian chlorites

Wt. %	1	2	3	4	5	6	7	8	9	10
Al_2O_3	15.23	15.37	11.99	14.25	10.56	9.29	10.83	7.96	10.78	16.84
SiO_2	32.20	31.58	32.25	33.87	33.50	33.99	32.93	32.73	34.15	30.82
Cr_2O_3	3.16	3.37	5.27	1.52	4.17	5.18	5.52	8.31	4.51	2.56
MgO	35.56	34.93	36.03	37.02	36.31	37.25	36.45	34.88	36.57	33.98
TiO_2	0.03	0.04	0.01	0.01	0.01	0.06	0.02	0.00	0.00	0.10
MnO	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.02	0.00	0.01
FeO*	1.19	1.42	0.95	0.83	1.62	1.20	1.36	2.29	0.77	2.25
NiO	0.24	0.20	0.09	0.16	0.14	0.22	0.08	0.00	0.34	0.16
H_2O**	12.39	13.10	13.40	12.34	13.70	12.81	12.81	13.82	12.87	13.28

1.	Day Book Body, North Carolina	$(Mg_{2.97}Al_{0.03})(Si_{3.02}Al_{0.98})O_{10}(OH)_2\cdot(Mg_{1.98}Al_{0.69}Cr_{0.23}Fe^{3+}_{0.04}Fe^{2+}_{0.04}Ni_{0.02})(OH)_6$
2.	Siskiyou Co., California	$(Mg_{2.95}Al_{0.05})(Si_{2.99}Al_{1.01})O_{10}(OH)_2\cdot(Mg_{1.97}Al_{0.66}Cr_{0.25}Fe^{3+}_{0.06}Fe^{2+}_{0.06})(OH)_6$
3.	Bilimbaievsk, Urals Mtns.	$(Mg_{3.00})(Si_{3.06}Al_{0.94})O_{10}(OH)_2\cdot(Mg_{2.10}Al_{0.41}Cr_{0.40}Fe^{3+}_{0.07}Ni_{0.01})(OH)_6$
4.	Lancaster Co., Pa.	$(Mg_{3.00})(Si_{3.14}Al_{0.86})O_{10}(OH)_2\cdot(Mg_{2.11}Al_{0.70}Cr_{0.11}Fe^{3+}_{0.07}Ni_{0.01})(OH)_6$
5.	Shetland Islands	$(Mg_{3.00})(Si_{3.19}Al_{0.81})O_{10}(OH)_2\cdot(Mg_{2.16}Al_{0.38}Cr_{0.32}Fe^{3+}_{0.13}Ni_{0.01})(OH)_6$
6.	Nuggihalli Schist Belt, India	$(Mg_{3.00})(Si_{3.21}Al_{0.79})O_{10}(OH)_2\cdot(Mg_{2.25}Al_{0.25}Cr_{0.39}Fe^{3+}_{0.09}Ni_{0.02})(OH)_6$
7.	Deer Creek, Wyoming	$(Mg_{3.00})(Si_{3.12}Al_{0.88})O_{10}(OH)_2\cdot(Mg_{2.14}Al_{0.33}Cr_{0.41}Fe^{3+}_{0.11}Ni_{0.01})(OH)_6$
8.	Gumushane, Turkey	$(Mg_{3.00})(Si_{3.19}Al_{0.81})O_{10}(OH)_2\cdot(Mg_{2.06}Al_{0.10}Cr_{0.64}Fe^{3+}_{0.09}Fe^{2+}_{0.10})(OH)_6$
9.	Ingessiah Hills, Sudan	$(Mg_{3.00})(Si_{3.23}Al_{0.77})O_{10}(OH)_2\cdot(Mg_{2.14}Al_{0.43}Cr_{0.34}Fe^{2+}_{0.06}Ni_{0.03})(OH)_6$
10.	San Benito Co., California	$(Mg_{3.00})(Si_{2.93}Al_{1.07})O_{10}(OH)_2\cdot(Mg_{1.80}Al_{0.82}Cr_{0.19}Fe^{3+}_{0.06}Fe^{2+}_{0.12}Ni_{0.01})(OH)_6$

* *All iron present shown as FeO.*

** *H_2O computed by difference.*

than that of the 2:1 octahedral sheet, which suggests the presence of the heavier atoms in the interlayer. Although the Lancaster chlorite shown in Figure 1 has the smallest number of heavy atoms by analysis, the contrast in peak heights is evident and allows quantitative evaluation. Electron counts were obtained by extrapolating the electron density peaks to the base line, integrating the areas, and scaling them to make one oxygen equal to nine electrons. The counts for the tetrahedral cations of the eight chlorites are all within one electron of the ideal value of 23.75 for two Si,Al cations (Table 2). This variation is less than the estimated error of extrapolation and integration, so that the presence of Cr^{3+} in tetrahedral coordination can be excluded for these specimens.

The electron counts for the 2:1 octahedral sheet indicate a composition close to $Mg_{3.00}$ (33 electrons for 50% ionization) for all eight specimens. All the octahedral trivalent cations and heavy atoms, therefore, must be concentrated in the interlayer sheet. The total of octahedral Al+Cr is generally smaller than the amount of tetrahedral Al, so that all the Fe found by microprobe analysis must be Fe^{3+} in five specimens and a mixture of Fe^{3+} and Fe^{2+} in two other specimens. The indicated compositions of the component sheets are listed in Table 1. The essential correctness of this allocation is indicated by two lines of evidence. Firstly, the electron counts calculated for the listed compositions compare favorably with the observed values (Table 2). Secondly, calculated electron density peak heights based on these compositions agree closely with the observed peak heights, as shown in Figure 1 for the Lancaster chlorite.

The one-dimensional projections and microprobe analyses indicate that the 2:1 layer of all eight chlorites is essentially that of ideal clinochlore $Mg_3(Si_{4-x}Al_x)O_{10}(OH)_2$ with $x = 0.77$ to 1.07. The tetrahedral charge is compensated entirely within the interlayer hydroxide sheet by a combination of Al, Cr, and Fe^{3+}. The Cr^{3+} ranges from 0.11 to 0.64 atoms per formula unit.

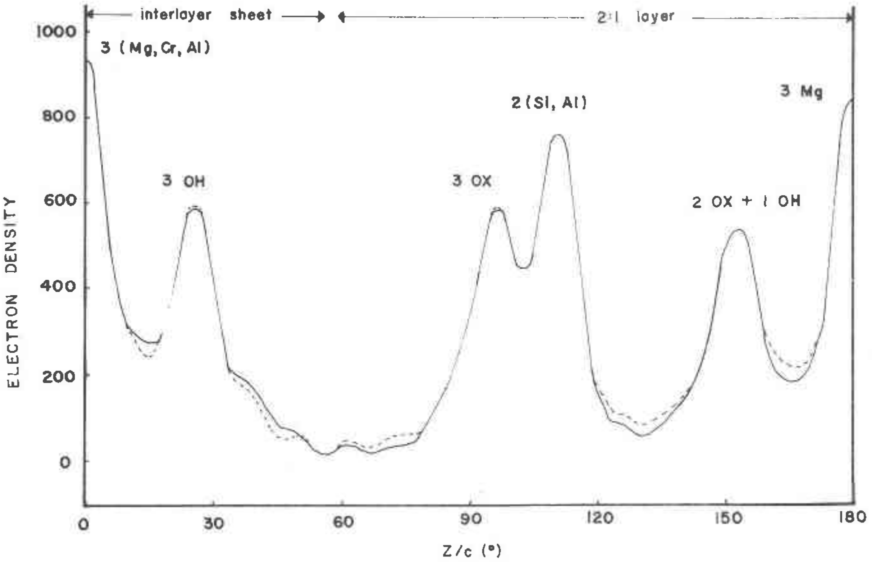

Fig. 1. One-dimensional electron density projection for chromian chlorite from Lancaster County, Pennsylvania. Calculated density is shown as dashed line, where not coincident with observed density.

Three-dimensional structural refinements

Experimental

Chromian chlorite crystals from the Day Book Body, North Carolina, and from Siskiyou County, California, were selected for detailed study because of their sharp reflections and lack of streaking of the $k \neq 3n$ reflections due to stacking faults. The Day Book Body chlorite, classified as kotschubeite by McCormick (1975) and kindly supplied by him, is pale violet in color and is found in dunite where it is intergrown with olivine and chromite. The crystals are optically positive with $2V$ ranging between 29° and 42°, and with refractive indices of $\alpha = \beta = 1.590(2)$ and $\gamma = 1.593(2)$. The single crystal selected for study was $0.35 \times 0.25 \times 0.005$ mm, and least-squares refinement of 13 medium-angle reflections on a Syntex P2_1 automated diffractometer yielded unit-cell parameters of $a = 5.327(2)$, $b = 9.227(4)$, $c = 14.356(6)$, $\alpha = 90.45(3)$, $\beta = 97.35(3)$, and $\gamma = 89.98(3)$. The Siskiyou County chlorite (NMNH #104723), donated both by Mrs. Davis Lapham and D. L. Bish and identified by Lapham (1958) as containing predominantly tetrahedral chromium, is uniaxial to biaxial positive with $2V$ ranging from 0° to 15°, and with refractive indices of $\alpha = 1.579$, $\beta = 1.580$, and $\gamma = 1.583$ (Lapham, 1958). The single crystal is $0.35 \times 0.25 \times 0.06$ mm, and least-squares refinement of 15 medium-angle reflections yielded unit-cell parameters of $a = 5.334(2)$, $b = 9.228(3)$, $c = 14.371(8)$A, $\alpha = 90.53(6)$, $\beta = 97.43(3)$, and $\gamma = 89.90(2)$.

Using graphite-monochromatized Mo$K\alpha$ radiation, 1441 and 1790 non-zero intensity reflections were collected from the Day Book Body and Siskiyou County crystals, respectively, in four quadrants of the limiting sphere from $2° < 2\theta < 90°$. The reflections were collected in the $2\theta : \theta$ variable-scan mode, and two standard reflections were monitored after every 50 reflections to check for crystal and electronic stability. Reflections were considered observed if $I > 2\sigma(I)$, where $I = [S - (B_1 + B_2)/B_r]T_r$, S being the scan count, B_1 and B_2 the background, B_r the ratio of background time to scan time, and T_r the 2θ scan rate in degrees per minute. $\sigma(I)$ was calculated from standard counting statistics. The reflections were corrected for Lorentz-polarization effects and empirically for absorption by comparing the data to complete Ψ scans (10° increments in ϕ) for selected reflections spaced at 5° intervals of 2θ. The structure amplitude values are given in Table 3.[2]

Refinement

Precession photographs of the Day Book Body and Siskiyou County chlorites showed them to be tri-

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[2] Table 3 may be obtained by ordering Document AM-80-122 from the Business Office, Mineralogical Society of America, 2000 Florida Ave., N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

Table 2. Electrons per cation plane from one-dimensional density projections

Sample location and source	Sheet	Electrons per formula unit	
		Calculated*	Observed
Bilimabaievsk Urals Mts., USSR (USNM #16261)	tetrahedral	24	25
	interlayer	39	39
	2:1 oct.	33	34
Low's Chromite Mine, Lancaster Co., Pa. (Wm. Penn Mem. Museum #M2628)	tetrahedral	24	25
	interlayer	36	35
	2:1 oct.	33	30
Setters, Unst, Shetland Islands (W.D. Christianson-Minerals #1.072.005)	tetrahedral	24	25
	interlayer	39	39
	2:1 oct.	33	32
Nuggihalli Schist Belt, India Damodaran and Somasekar, 1976)	tetrahedral	24	23
	interlayer	39	35
	2:1 oct.	33	33
Deer Creek, Wyoming (USNM #93908)	tetrahedral	24	23
	interlayer	40	41
	2:1 oct.	33	30
Gumushane, Turkey (David New-Minerals)	tetrahedral	24	25
	interlayer	43	41
	2:1 oct.	33	31
Ingessiah Hills, Sudan (A. Al Mishwt)	tetrahedral	24	23
	interlayer	41	39
	2:1 oct.	33	29
San Benito Co., Calif. (David New-Minerals)	tetrahedral	24	23
	interlayer	38	39
	2:1 oct.	33	34

Calculated from the microprobe analyses, assuming 50% ionization and all octahedral trivalent cations and heavy atoms concentrated in the interlayer.

clinic, and by comparison with photographs of other chlorites they were found to be of the polytype II*b*-4. As a first step the ideal coordinates given in Bailey and Brown (1962) in space group $C\bar{1}$ were refined by the least-squares program ORFLS. With the results of the microprobe analyses (Table 1), scattering factors were calculated from the values reported in *International Tables for X-ray Crystallography* (1962) under the assumption of half-ionization of the atoms and cation disorder over the available sites. The sense of the Z axis was determined by comparison of F_o and F_c values. Using unit weights, the residual R_1 converged to 6.3% (wR = 7.1%) for the Day Book Body chlorite, and to 6.3% (wR = 7.0%) for the Siskiyou County chlorite. At this stage of refinement, bond lengths for both structures indicated that Cr^{3+} and Al were concentrated in interlayer octahedral site M(4), while no ordering of Al occurred between the two independent tetrahedral sites.

Although no tetrahedral ordering was indicated in space group $C\bar{1}$, ordering of Al still could possibly occur in sub-group symmetry $C1$. To test this possibility, four tetrahedral ordering models were postulated that would be ordered in symmetry $C1$ but disordered in $C\bar{1}$. Because of the high degree of pseudosymmetry that occurs when the $C1$ atom parameters are derived by expanding the $C\bar{1}$ parameters over the inversion centers, the pseudosymmetry-related atoms must first be moved off their symmetry-related positions before refinement in $C1$ can begin. This was done by the distance least squares program OPTDIS of W. A. Dollase (University of California, Los Angeles), which produced a set of approximate atomic coordinates for each of the four tetrahedral ordering models. Subsequent refinement of the four models in each of the structures by ORFLS showed that, although the problem of high correlations had been removed, the R factors and atomic coordinates failed to converge for these models, indicating the space group $C1$ to be incorrect. Successive least-squares cycles on individual models resulted in atomic coordinates with tetrahedral bond distances trending toward disorder, *i.e.* the postulated smaller Si sites became larger, while the postulated larger Al-rich sites became smaller. All four ordering models were rejected, therefore, and the structure was assumed to be tetrahedrally disordered in space group $C\bar{1}$.

The final refinement of each structure in space group $C\bar{1}$ consisted of alternating cycles of electron-density difference maps and least-squares refinement. Cation site occupancies were adjusted after each cycle until a flat difference map was obtained. The difference maps proved to be very sensitive to small changes in the heavy-atom concentration. Least-squares refinement of the Siskiyou County structure was done with ORFLS, while refinement of the Day Book Body structure was done using both ORFLS and program RFINE (Finger and Prince, 1975). The same values of cation site occupancies (Table 7) were obtained for the Day Book Body chlorite by using difference maps to adjust occupancies and by using RFINE to constrain the occupancies to the microprobe composition. Seventeen low-angle reflections indicated by RFINE to have anomalous extinction factors were removed from the data set of the Day Book Body chlorite, and subsequent refinement with anisotropic thermal parameters with Al, Cr, and other heavy atoms ordered in M(4) reduced the R factor from 6.3% to 6.0% (wR = 6.3%). Similar refinement of the Siskiyou County structure with ORFLS reduced the R factor from 6.3% to 5.9% (wR = 7.0%).

At this stage of the refinement the four hydrogen atoms were searched for and found in each of the structures on electron-density difference maps. Atomic coordinates for the four hydrogen positions were calculated using Booth's (1948, p. 62–65) method for location of electron density maxima, and these unrefined coordinates are reported in Table 4 for the Siskiyou County structure as they yield reasonable bond lengths (whereas subsequent ORFLS refinement of the hydrogen positions moved the atoms unreasonably close to the oxygen atoms to which they were bonded). On the other hand, the H–O bond distances of the Day Book Body structure lengthened slightly upon refinement to become more reasonable, and thus the refined hydrogen atom coordinates are listed in Table 4 for this specimen. By comparing the heights of the hydrogen peaks, which were about 2.5 times the background, to the height of an oxygen peak that had been deliberately left out of one round of refinement, the atoms H(1), H(2), H(3), and H(4) of the Day Book Body and Siskiyou County structures were found to represent 0.24, 0.41, 0.37, 0.51 and 0.53, 0.34, 0.40, 0.45 electrons respectively. When these four atoms were incorporated into the least-squares refinement (but were not varied in the Siskiyou County structure) the residual decreased from 6.0% to 5.9% ($wR = 6.2\%$) for the Day Book Body structure, and decreased from 5.9% to 5.6% ($wR = 6.6\%$) for the Siskiyou County structure.

Discussion

Some important structural features are shown in Table 5, and the calculated bond lengths and angles are listed in Table 6. Comparison of the refined

Table 4. Final atomic coordinates and temperature factors

Atom	x	y	z	iso. B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
					Day Book Body, N. C.					
M(1)	0.0000	0.0000	0.0000	1.40(6)	0.0091(6)	0.0042(3)	0.0029(1)	-0.0004(3)	0.0007(2)	0.0002(1)
M(2)	0.0015(3)	0.3336(2)	-0.0001(1)	1.41(5)	0.0089(4)	0.0041(2)	0.00298(8)	-0.0006(2)	0.0006(1)	0.00012(8)
M(3)	-0.0008(3)	0.1667(2)	0.4999(1)	1.49(5)	0.0109(5)	0.0043(2)	0.00332(8)	-0.0008(2)	0.0006(2)	0.00018(9)
M(4)	0.0000	0.5000	0.5000	1.10(5)	0.0057(5)	0.0023(2)	0.00224(9)	-0.0008(2)	0.0005(2)	0.0002(1)
T(1)	0.2328(2)	0.1688(1)	0.1920(1)	0.81(4)	0.0040(4)	0.0019(2)	0.00214(8)	-0.0007(2)	0.0004(1)	0.00016(8)
T(2)	0.7332(2)	0.0022(1)	0.1919(1)	0.81(4)	0.0037(4)	0.0020(2)	0.00215(8)	-0.0005(2)	0.0003(1)	0.00018(8)
OH(1)	0.6915(6)	0.3338(4)	0.0727(3)	1.02(9)	0.006(1)	0.0033(4)	0.0023(2)	-0.0002(5)	0.0004(3)	0.0003(2)
OH(2)	0.1582(7)	-0.0009(4)	0.4305(3)	1.46(10)	0.011(1)	0.0042(4)	0.0022(2)	-0.0011(6)	0.0001(4)	0.0002(2)
OH(3)	0.1349(7)	0.3396(4)	0.4303(2)	1.43(10)	0.012(1)	0.0042(4)	0.0022(2)	-0.0008(5)	0.0005(4)	0.0004(2)
OH(4)	0.6351(7)	0.1582(4)	0.4308(3)	1.44(10)	0.009(1)	0.0038(4)	0.0022(2)	-0.0003(5)	-0.0002(4)	0.0001(2)
O(1)	0.1935(6)	0.1673(4)	0.0769(3)	0.99(9)	0.005(1)	0.0029(4)	0.0024(2)	-0.0008(5)	0.0006(3)	0.0004(2)
O(2)	0.6938(6)	0.0011(4)	0.0767(3)	1.03(9)	0.006(1)	0.0025(4)	0.0023(2)	-0.0009(5)	0.0005(3)	0.0000(2)
O(3)	0.2107(7)	0.3364(4)	0.2333(3)	1.5(1)	0.013(1)	0.0040(4)	0.0026(2)	-0.0013(6)	0.0004(4)	0.0003(2)
O(4)	0.5151(7)	0.1045(4)	0.2334(3)	1.4(1)	0.010(1)	0.0040(4)	0.0030(2)	-0.0001(5)	0.0003(4)	-0.0002(2)
O(5)	0.0148(7)	0.0674(4)	0.2330(3)	1.5(1)	0.009(1)	0.0052(5)	0.0030(2)	-0.0017(6)	0.0003(4)	0.0007(2)
H(1)	0.687(16)	0.343(9)	0.142(6)	1.5						
H(2)	0.127(16)	0.012(9)	0.371(6)	1.5						
H(3)	0.129(16)	0.351(9)	0.367(6)	1.5						
H(4)	0.608(16)	0.157(9)	0.368(6)	1.5						
					Siskiyou Co., Calif.					
M(1)	0.0000	0.0000	0.0000	1.12(4)	0.0116(6)	0.0037(2)	0.00109(8)	0.0019(3)	0.0000(2)	-0.0001(1)
M(2)	0.0014(3)	0.3337(2)	0.0000(1)	1.13(3)	0.0115(4)	0.0038(2)	0.00108(6)	0.0017(2)	0.0000(1)	-0.00019(6)
M(3)	-0.0006(3)	0.1667(2)	0.5000(1)	1.37(3)	0.0136(5)	0.0045(2)	0.00141(6)	0.0019(2)	0.0005(1)	-0.00001(8)
M(4)	0.0000	0.5000	0.5000	1.05(3)	0.0112(5)	0.0035(2)	0.00100(7)	0.0016(2)	0.0002(1)	-0.00004(9)
T(1)	0.2326(2)	0.1692(1)	0.1920(1)	0.79(3)	0.0088(4)	0.0029(2)	0.00065(5)	0.0018(2)	0.0001(1)	-0.00001(6)
T(2)	0.7331(2)	0.0023(1)	0.1919(1)	0.81(3)	0.0091(4)	0.0029(1)	0.00069(5)	0.0017(2)	0.0001(1)	-0.00001(6)
OH(1)	0.6923(6)	0.3339(4)	0.0731(2)	1.02(6)	0.012(1)	0.0036(4)	0.0007(1)	0.0025(5)	0.0000(3)	0.0001(2)
OH(2)	0.1575(7)	-0.0011(4)	0.4302(2)	1.26(7)	0.016(1)	0.0052(4)	0.0006(1)	0.0026(5)	0.0002(3)	0.0001(2)
OH(3)	0.1334(6)	0.3402(4)	0.4301(2)	1.27(7)	0.014(1)	0.0053(4)	0.0008(1)	0.0025(5)	0.0003(3)	0.0002(2)
OH(4)	0.6335(6)	0.1570(4)	0.4307(2)	1.23(7)	0.012(1)	0.0055(4)	0.0008(1)	0.0028(5)	0.0000(3)	0.0000(2)
O(1)	0.1932(6)	0.1675(4)	0.0766(2)	0.92(6)	0.010(1)	0.0031(4)	0.0008(1)	0.0023(5)	0.0001(3)	0.0001(20
O(2)	0.6930(6)	0.0009(4)	0.0766(2)	0.94(6)	0.011(1)	0.0033(4)	0.0009(1)	0.0024(5)	0.0003(3)	0.0000(2)
O(3)	0.2108(7)	0.3367(4)	0.2331(2)	1.54(7)	0.020(1)	0.0050(4)	0.0010(1)	0.0007(6)	-0.0001(3)	-0.0002(2)
O(4)	0.5162(7)	0.1045(4)	0.2340(2)	1.50(7)	0.016(1)	0.0066(5)	0.0010(1)	0.0025(6)	-0.0002(3)	-0.0004(2)
O(5)	0.0164(7)	0.0682(4)	0.2330(2)	1.55(7)	0.015(1)	0.0065(5)	0.0010(1)	-0.0001(6)	-0.0002(3)	0.0002(2)
H(1)	0.7054	0.3318	0.1375	1.5						
H(2)	0.1521	0.0027	0.3625	1.5						
H(3)	0.1320	0.3445	0.3635	1.5						
H(4)	0.6125	0.1527	0.3617	1.5						

Table 5. Important structural features

Parameter	Day Book Body, North Carolina	Siskiyou Co., California
Tetrahedral rotation[a] α_{tet}(°)	7.2	6.0
Tetrahedral angle[b] τ_{tet}(°)	T(1): 110.7 T(2): 110.8	T(1): 110.8 T(2): 111.0
Octahedral flattening[c] ψ_{oct}(°)	M(1), M(2): 58.8 M(3): 61.5 M(4): 59.8	M(1), M(2): 58.0 M(3): 61.2 M(4): 59.4
Octahedral distortion[d]	rms(°) (σ_θ)	rms(°) (σ_θ)
	M(1): 5.6 40.3 M(2): 4.9 31.9 M(3): 8.5 94.0 M(4): 6.9 55.3	M(1): 5.7 34.9 M(2): 5.7 34.9 M(3): 9.3 93.9 M(4): 6.6 48.0
Sheet Thickness (Å)		
tetrahedral	2.247	2.251
2:1 octahedral	2.147	2.150
interlayer	1.976	1.986
Interlayer separation	2.810	2.807
Δz_{ave} Basal oxygen (Å)	0.005	0.014
β_{ideal}[e](°)	97.11	97.11

[a] *Calculated from* $\alpha = 1/2 \mid 120° - \text{mean } O_b\text{-}O_b\text{-}O_b \text{ angle} \mid$.

[b] *Defined as* $\tau = O_{apical}\text{--}T\text{--}O_{basal}$. *The ideal value is 109.47°.*

[c] *The mean octahedral angle calculated from* $\cos\psi$ *- oct. thickness divided by 2* $(\overline{M\text{--}O,OH})$ *Ideal value is 54.73°.*

[d] *RMS octahedral distortion parameter is defined by Dollase (1969) as the rms-deviation of the 15 octahedral angles from their ideal values.* (σ_θ) *is defined by Robinson et al. (1971) as* $(\sigma_\theta)^2 = \sum_{i=1}^{12}(\theta_i-90)^2/11$, *where* θ_i *is the observed O--M--O angle.*

[e] $\beta_{ideal} = 180° - \cos^{-1}(\underline{a}/3c)$.

atomic positions of the two structures with the ideal positions given in Bailey and Brown (1962) shows that cation substitution and ordering have produced distortions in the structure. Preferential ordering of the trivalent cations into the interlayer M(4) site has produced a smaller octahedron and is believed to be responsible also for the triclinic cell angle α. The individual octahedra are flattened and distorted to differing extents. The tetrahedra have rotated to form ditrigonal rings in which the basal oxygens approach more closely the octahedral cations in the 2:1 layer as well as the interlayer hydroxyls. Inspection of the *z* coordinates in Table 4 shows that both O(4) and OH(4) have been raised slightly above their respective anion planes, an effect more pronounced in the Siskiyou County specimen. This is thought to be caused by attraction between the O(4) anion (whose charge, due to Al^{IV} substitution, is not fully satisfied) and the trivalent cations in the M(4) interlayer site above. As O(4) is raised, anion–anion repulsion would tend also to raise the overlying OH(4) hydroxyl, in effect "keying" the structure together slightly. As O(4) is the closest of the basal oxygens to M(4), it would be attracted to the greatest extent.

Cation ordering

The mean bond lengths listed in Table 6 indicate the nature of the cation ordering occurring in both structures. Site M(4) is considerably smaller than the other three octahedral sites, indicating that the trivalent Al, Cr, and Fe^{3+} are preferentially located here. Electron density difference maps indicate that the small amounts of Fe^{2+} and Ni present also are in this site. The mean bond lengths of the two independent tetrahedra are identical, indicating that no ordering of Al^{IV} occurs. Table 7 lists the observed mean bond lengths involving the six cations, along with the bond lengths calculated for the cation occupancy that has been allocated to each site on the basis of the structure determinations and the microprobe analyses. The calculated and observed mean bond lengths are very close for the tetrahedral sites and within 0.01A for octahedral sites M(1) to M(3) in both structures, with the effective ionic radii of Shannon (1976). The calculated distances for M(4), however, are 0.03 to 0.04A shorter than the observed values. This should not be taken as evidence for a larger cation in M(4), as the deviation is due to the pattern of shared edges within the ordered interlayer sheet.

M(4) containing the trivalent interlayer cations lies on an inversion center and is surrounded symmetrically by a hexagon of M(3) octahedra containing Mg. The M(3) octahedra are larger than the M(4) octahedron and are severely flattened (ψ = 61.2°, 61.5°, Table 5) and distorted [$(\sigma_\theta)^2$ = 93.9, 94.0, Table 5] in order to fit onto the smaller and more regular M(4) octahedron [ψ = 59.4°, 59.8° and $(\sigma_\theta)^2$ = 48.0, 55.3]. The distortion of M(3) octahedra arises from having to share diagonal edges both with each other and with M(4), whereas M(4) shares edges only with M(3) in a symmetrical manner. The OH groups on these latter shared edges also are parts of shared edges between adjacent M(3) octahedra, however, and cannot approach the M(4) cation more closely without distorting M(3) octahedra to an even greater extent. In a laterally unconstrained octahedral sheet, such as in a mica, deviations of this sort from ideality can be eliminated by lateral shortening of cell edges, but in a chlorite the interlayer must remain extended laterally in order to bond effectively with trioctahedral 2:1 layers above and below. Observed M(4)–OH bonds therefore remain appreciably longer than ideal.

The Cr^{3+} and other octahedral trivalent cations provide the excess positive charge required to balance the negative charge due to substitution of Al^{IV}

Table 6. Calculated bond lengths and angles

Day Book Body, N. C.						Siskiyou Co., Calif.					
Bond Lengths (A)				Bond Angles ( )		Bond Lengths (A)				Bond Angles ( )	
		Tetrahedron T(1)						Tetrahedron T(1)			
O(1)	1.639(4)	O(1)--O(3)	2.716(6)	O(1)--O(3)	110.9(2)	O(1)	1.645(3)	O(1)--O(3)	2.718(5)	O(1)--O(3)	110.7(2)
O(3)	1.661(4)	O(4)	2.713(5)	O(4)	110.8(2)	O(3)	1.659(4)	O(4)	2.727(5)	O(4)	110.9(2)
O(4)	1.657(4)	O(5)	2.712(5)	O(5)	110.6(2)	O(4)	1.667(4)	O(5)	2.716(5)	O(5)	110.8(2)
O(5)	1.660(4)	O(3)--O(4)	2.684(6)	O(3)--O(4)	108.0(2)	O(5)	1.654(4)	O(3)--O(4)	2.689(5)	O(3)--O(4)	107.9(2)
Mean	1.654	O(5)	2.693(6)	O(5)	108.4(2)	Mean	1.656	O(5)	2.688(6)	O(5)	108.4(2)
		O(4)--O(5)	2.686(5)	O(4)--O(5)	108.2(2)			O(4)--O(5)	2.686(5)	O(4)--O(5)	108.0(2)
		Mean	2.701	Mean	109.5			Mean	2.704	Mean	109.5
		Tetrahedron T(2)						Tetrahedron T(2)			
O(2)	1.641(4)	O(2)--O(3)	2.716(5)	O(2)--O(3)	111.0(2)	O(2)	1.644(4)	O(2)--O(3)	2.716(5)	O(2)--O(3)	110.9(2)
O(3)	1.655(4)	O(4)	2.719(6)	O(4)	110.8(2)	O(3)	1.654(4)	O(4)	2.726(5)	O(4)	111.1(2)
O(4)	1.663(4)	O(5)	2.707(5)	O(5)	110.6(2)	O(4)	1.662(4)	O(5)	2.718(5)	O(5)	110.6(2)
O(5)	1.652(4)	O(3)--O(4)	2.684(6)	O(3)--O(4)	108.0(2)	O(5)	1.664(4)	O(3)--O(4)	2.680(5)	O(3)--O(4)	107.8(2)
Mean	1.653	O(5)	2.678(5)	O(5)	108.2(2)	Mean	1.656	O(5)	2.690(5)	O(5)	108.3(2)
		O(4)--O(5)	2.685(5)	O(4)--O(5)	108.2(2)			O(4)--O(5)	2.690(5)	O(4)--O(5)	108.0(2)
		Mean	2.698	Mean	109.5			Mean	2.703	Mean	109.5
		Octahedron M(1)						Octahedron M(1)			
O(1)x2	2.082(4)	O(1)--O(2)x2	3.072(5)	O(1)--O(2)x2	95.0(1)	O(1)x2	2.085(3)	O(1)--O(2)x2	3.082(5)	O(1)--O(2)x2	95.2(1)
O(2)x2	2.085(4)	OH(1)x2	3.077(5)	OH(1)x2	95.9(1)	O(2)x2	2.088(3)	OH(1)x2	3.078(5)	OH(1)x2	95.9(2)
OH(1)x2	2.057(4)	O(2)-OH(1)x2	3.074(5)	O(2)-OH(1)x2	95.9(1)	OH(1)x2	2.062(3)	O(2)-OH(1)x2	3.080(5)	O(2)-OH(1)x2	95.9(1)
Mean	2.075	Mean (unshared)	3.074	Mean (unshared)	95.6	Mean	2.078	Mean (unshared)	3.080	Mean (unshared)	95.7
		O(1)--O(2)x2	2.814(5)	O(1)--O(2)x2	85.0(2)			O(1)--O(2)x2	2.813(5)	O(1)--O(2)x2	84.8(2)
		OH(1)x2	2.773(5)	OH(1)x2	84.1(1)			OH(1)x2	2.778(5)	OH(1)x2	84.1(1)
		O(2)-OH(1)x2	2.771(5)	O(2)-OH(1)x2	84.1(1)			O(2)-OH(1)x2	2.781(5)	O(2)-OH(1)x2	84.1(1)
		Mean (shared)	2.786	Mean (shared)	84.4			Mean (shared)	2.791	Mean (shared)	84.3
		Octahedron M(2)*						Octahedron M(2)*			
O(1)	2.088(4)	O(1)--O(2)	3.080(5)	O(1)--O(2)	95.2(2)	O(1)	2.085(4)	O(1)--O(2)	3.077(5)	O(1)--O(2)	95.3(1)
O(2)	2.083(4)	OH(1)	3.078(5)	OH(1)	95.7(2)	O(2)	2.078(4)	OH(1)	3.075(5)	OH(1)	95.6(1)
OH(1)	2.065(4)	O(2)-OH(1)	3.083(5)	O(2)-OH(1)	96.0(2)	OH(1)	2.067(4)	O(2)-OH(1)	3.081(5)	O(2)-OH(1)	96.0(1)
O(1A)	2.076(4)	O(1A)-O(2A)	3.075(5)	O(1A)-O(2A)	95.3(2)	O(1A)	2.081(4)	O(1A)-O(2A)	3.076(5)	O(1A)-O(2A)	95.2(1)
O(2A)	2.085(4)	OH(1A)	3.074(5)	OH(1A)	96.1(2)	O(2A)	2.085(4)	OH(1A)	3.082(5)	OH(1A)	96.1(1)
OH(1A)	2.057(4)	O(2A)-OH(1A)	3.071(5)	O(2A)-OH((A)	95.7(2)	OH(1A)	2.065(4)	O(2A)-OH(1A)	3.075(5)	O(2A)-OH(1A)	95.6(1)
Mean	2.076	Mean (unshared)	3.077	Mean (unshared)	95.7	Mean	2.077	Mean (unshared)	3.078	Mean (unshared)	95.6
		O(1)--O(1A)	2.821(7)	O(1)--O(1A)	85.3(2)			O(1)--O(1A)	2.818(6)	O(1)--O(1A)	85.1(1)
		OH(1A)	2.773(5)	OH(1A)	84.0(2)			OH(1A)	2.778(4)	OH(1A)	84.0(1)
		O(2)--O(1A)	2.814(5)	O(2)--O(1A)	85.2(2)			O(2)--O(1A)	2.813(5)	O(2)--O(1A)	85.1(1)
		O(2A)	2.819(7)	O(2A)	85.1(2)			O(2A)	2.814(6)	O(2A)	85.0(1)
		OH(1)--O(2A)	2.771(5)	OH(1)-O(2A)	83.8(2)			OH(1)--O(2A)	2.781(5)	OH(1)--O(2A)	84.1(1)
		OH(1A)	2.724(8)	OH(1A)	82.7(2)			OH(1A)	2.733(6)	OH(1A)	82.8(1)
		Mean (shared)	2.787	Mean (shared)	84.4			Mean (shared)	2.790	Mean (shared)	84.4
		Octahedron M(3)*						Octahedron M(3)*			
OH(2)	2.072(4)	OH(2)-OH(3)	3.145(6)	OH(2)-OH(3)	98.8(2)	OH(2)	2.074(4)	OH(2)-OH(3)	3.154(5)	OH(2)-OH(3)	99.0(2)
OH(2A)	2.068(4)	OH(4)	3.150(5)	OH(4)	99.2(2)	OH(2A)	2.072(4)	OH(4)	3.152(5)	OH(4)	98.9(2)
OH(3)	2.069(4)	OH(2A)-OH(3A)	3.152(5)	OH(2A)-OH(3A)	99.1(2)	OH(3)	2.075(4)	OH(2A)-OH(3A)	3.158(5)	OH(2A)-OH(3A)	98.9(2)
OH(3A)	2.075(4)	OH(4A)	3.147(5)	OH(4A)	99.2(2)	OH(3A)	2.084(4)	OH(4A)	3.157(5)	OH(4A)	99.3(2)
OH(4)	2.064(4)	OH(3)-OH(4)	3.146(5)	OH(3)-OH(4)	99.2(2)	OH(4)	2.075(4)	OH(3)-OH(4)	3.161(5)	OH(3)-OH(4)	99.3(2)
OH(4A)	2.065(4)	OH(3A)-OH(4A)	3.145(5)	OH(3A)-OH(4A)	98.9(2)	OH(4A)	2.071(4)	OH(3A)-OH(4A)	3.155(5)	OH(3A)-OH(4A)	98.8(2)
Mean	2.069	Mean (unshared)	3.148	Mean (unshared)	99.1	Mean	2.075	Mean (unshared)	3.156	Mean (unshared)	99.0
		OH(2)-OH(2A)	2.771(8)	OH(2)-OH(2A)	84.0(2)			OH(2)-OH(2A)	2.778(7)	OH(2)-OH(2A)	84.1(2)
		OH(3A)	2.610(5)	OH(3Q)	78.0(2)			OH(3A)	2.616(5)	OH(3A)	78.0(2)
		OH(3)-OH(3A)	2.769(8)	OH(3)-OH(3A)	83.9(2)			OH(3)-OH(3A)	2.787(7)	OH(3)-OH(3A)	84.2(2)
		OH(4A)	2.603(5)	OH(4A)	78.1(2)			OH(4A)	2.601(5)	OH(4A)	77.7(2)
		OH(4)-OH(4A)	2.763(8)	OH(4)-OH(4A)	84.0(2)			OH(4)-OH(4A)	2.785(7)	OH(4A)	84.4(2)
		OH(2A)	2.601(5)	OH(2A)	78.0(2)			OH(2A)	2.603(5)	OH(4)-OH(2A)	77.8(2)
		Mean (shared)	2.686	Mean (shared)	81.0			Mean (shared)	2.695	Mean (shared)	81.0

for Si. In all 10 chlorites of this study the octahedral trivalent cations have segregated in the interlayer sheet. Theoretically some of these trivalent cations could go in the 2:1 octahedral sheet, where they would be closer to the source of negative charge on the tetrahedral sheets, but they do not do so. The interlayer sheet requires an overall positive charge for its stability, and this is provided by substitution of R^{3+} for R^{2+} in that sheet. It is likely that only the R^{3+} in excess of the amount required for interlayer stabil-

Table 6. (continued)

Day Book Body, N. C.						Siskiyou Co., Calif.					
Bond Lengths (Å)				Bond Angles (°)		Bond Lengths (Å)				Bond Angles (°)	
Octahedron M(4)						Octahedron M(4)					
OH(2)	1.961(4)	OH(2)-OH(3)x2	2.935(5)	OH(2)-OH(3)x2	96.7(2)	OH(2)x2	1.967(4)	OH(2)-OH(3)x2	2.928(5)	OH(2)-OH(3)x2	96.4(1)
OH(3)x2	1.967(4)	OH(4)x2	2.934(5)	OH(4)x2	96.9(2)	OH(3)x2	1.960(4)	OH(4)x2	2.931(5)	OH(4)x2	96.8(1)
OH(4)x2	1.960(4)	OH(3)-OH(4)x2	2.940(6)	OH(3)-OH(4)x2	97.0(2)	OH(4)x2	1.953(4)	OH(3)-OH(4)x2	2.923(5)	OH(3)-OH(4)x2	96.7(1)
Mean	1.963	Mean (unshared)	2.936	Mean (unshared)	96.9	Mean	1.960	Mean (unshared)	2.927	Mean (unshared)	96.6
		OH(2)-OH(3)x2	2.610(5)	OH(2)-OH(3)x2	83.3(2)			OH(2)-OH(3)x2	2.616(5)	OH(2)-OH(3)x2	83.6(2)
		OH(4)x2	2.601(5)	OH(4)x2	83.1(2)			OH(4)x2	2.603(5)	OH(4)x2	83.2(2)
		OH(3)-OH(4)x2	2.603(5)	OH(3)-OH(4)x2	83.0(2)			OH(3)-OH(4)x2	2.601(5)	OH(3)-OH(4)x2	83.2(2)
		Mean (shared)	2.605	Mean (shared)	83.1			Mean (shared)	2.607	Mean (shared)	83.3
Hydrogen Bonds						Hydrogen Bonds					
		H(1)-OH(1)	0.998(4)					H(1)-OH(1)	0.913(3)		
		H(2)-OH(2)	0.854(4)	O(5)-H(2)-OH(2)	171.5(3)			H(2)-OH(2)	0.971(3)	O(5)-H(2)-OH(2)	154.8(2)
		OH(2)--O(5)	2.915(6)					OH(2)--O(5)	2.914(5)		
		H(3)-OH(3)	0.915(4)	O(3)-H(3)-OH(3)	162.5(2)			H(3)-OH(3)	0.958(3)	O(3)-H(3)-OH(3)	166.6(2)
		OH(3)--O(3)	2.907(6)					OH(3)--O(3)	2.913(5)		
		H(4)-OH(4)	0.899(4)	O(4)-H(4)-OH(4)	165.3(3)			H(4)-OH(4)	0.984(3)	O(4)-H(4)-OH(4)	165.3(3)
		OH(4)--O(4)	2.893(6)					OH(4)--O(4)	2.852(5)		
Interlayer Cation to Tetrahedral Cation*						Interlayer Cation to Tetrahedral Cation*					
		ideal**						ideal**			
M(3)--T(1)	4.709(3)	4.741				M(3)--T(1)	4.708(3)	4.741			
T(1A)	4.744(3)	4.741				T(1A)	4.751(3)	4.741			
T(2)	4.745(3)	4.737				T(2)	4.749(3)	4.737			
T(2A)	4.707(3)	4.737				T(2A)	4.709(3)	4.737			
Mean	4.726					Mean	4.729				
		ideal**						ideal**			
M(4)--T(1)	4.744(2)	4.737				M(4)--T(1)	4.749(2)	4.737			
T(1A)	4.744(2)	4.737				T(1A)	4.749(2)	4.737			
T(2)	4.744(2)	4.741				T(2)	4.751(2)	4.741			
T(2A)	4.744(2)	4.741				T(2A)	4.751(2)	4.741			
Mean	4.744					Mean	4.750				

* *Atoms such as X(1A) are related to X(1) atoms by an inversion center.*

** *Ideal M--T distances calculated using ideal atomic coordinates for polytype II*__b__*-4 in Bailey and Brown (1962).*

ity will enter the 2:1 octahedral sheet. This does not happen in these chlorites because the layer charges are all smaller than the average charge of −1.31 found in a survey of 111 II*b* chlorites by Bailey and Brown (1962).

Two factors are thought to play a part in localizing the Cr^{3+} in the M(4) site within the interlayer:

(1) Minimization of cation repulsion would tend to localize the Cr^{3+} and other trivalent cations in the M(4) site, as M(4) is farther away from the Si,Al ions in the tetrahedral sheets above and below the interlayer than is M(3). Although in the ideal chlorite structure these two sites are equidistant from the Si,Al cations, the actual structure is distorted by a small displacement of 2:1 layers on opposite sides of the interlayer that appears to be due to repulsion by M(4). This would not be the case if the Cr^{3+} segregated into the M(3) sites because the geometry of superposition of layers around M(3) is quite different. This effect is illustrated in Figure 2, and the M–T bond lengths involved are shown in Table 6.

(2) As a cooperative effect, in addition to the charge minimization effect above, the transition metals would gain additional stability in the same octahedral site as Al because of the smaller size of that octahedron. The crystal field splitting parameter will be considerably larger because of the smaller average size of the M(4) cation. Although M(4) is a more regular octahedron than M(3) (Table 5), this factor should have no influence on the distribution of Cr^{3+}, Fe^{3+}, or Ni^{2+} because of their lack of preference for regular or distorted octahedral sites (Burns, 1970).

The mean tetrahedral bond lengths in Table 7 show that no ordering of Al occurs between the two independent tetrahedra and, as discussed previously, refinement of four possible tetrahedral ordering models in a lower symmetry also yielded no evidence of ordering. As shown in Figure 2, the tetrahedra are

Table 7. Cation site occupancies and bond lengths

Site	Cation	Calculated* Bond Length (Å)	Observed Mean Bond Length (Å)
	Day Book Body, N. C.		
M(1)	$Mg_{.99}Al_{.01}$	2.088	2.075
M(2)	$Mg_{.99}Al_{.01}$	2.088	2.075
M(3)	$Mg_{.99}Al_{.01}$	2.068	2.069
M(4)	$Al_{.67}Cr_{.23}Fe^{3+}_{.04}Fe^{2+}_{.04}Ni_{.02}$	1.920	1.963
T(1),T(2)	$Si_{.76}Al_{.24}$	1.655	1.654
	Siskiyou Co., Calif.		
M(1)	$Mg_{.98}Al_{.02}$	2.087	2.078
M(2)	$Mg_{.98}Al_{.02}$	2.087	2.076
M(3)	$Mg_{.98}Al_{.02}$	2.067	2.075
M(4)	$Al_{.62}Cr_{.25}Fe^{3+}_{.06}Fe^{2+}_{.06}Ni_{.01}$	1.929	1.960
T(1),T(2)	$Si_{.75}Al_{.25}$	1.656	1.656

*M--O bond lengths calculated from the radii of Shannon (1976). T--O bond lengths calculated from equation 1 in Baur (1978).

approximately equidistant from the trivalent M(4) site, and thus no driving force for ordering due to charge balance exists [in contrast to the I*a* chlorite configuration of layer–interlayer, where ordering of tetrahedral Al produces local charge balance (Brown and Bailey, 1963)]. For the II*b*-4 polytype a disordered tetrahedral Si,Al distribution provides the most favorable balance of charge around M(4).

Triclinicity

One surprising aspect of this study was the observed value for the cell angle α (90.45° and 90.53°, respectively, for the Day Book Body and Siskiyou County chlorites). This triclinic slewing of the structure has not been reported for chlorites before. It is proposed that cation repulsion between the tetrahedral cations and the trivalent cations in the M(4) interlayer site offsets the tetrahedral sheets above and below the interlayer so that the cell angles α and β are increased relative to their ideal values (Fig. 2). We have suggested already that the capability of distorting the structure in this manner is one of the reasons the trivalent interlayer cations prefer to locate in M(4). After the slewing effect the mean M(4)–T distance is significantly greater than the mean M(3)–T distance (Table 6). The two shortest distances around the M(3) site are to be expected as they are on the line of direction of offset of the tetrahedral sheets. A rough calculation shows that the offset of the tetrahedral cations along *Y* [derived by subtracting the observed *y* coordinate of T(1) from the ideal coordinate given in Bailey and Brown (1962)] is of the same order of magnitude, when projected over the entire *Z* distance, as the observed offset of the entire structure along *Y* (0.11A calculated *vs.* 0.13A observed). From this it is evident that the magnitude of the offset along *Y* (and thus the α angle) can be accounted for solely by the cation repulsion effect. Observation of a

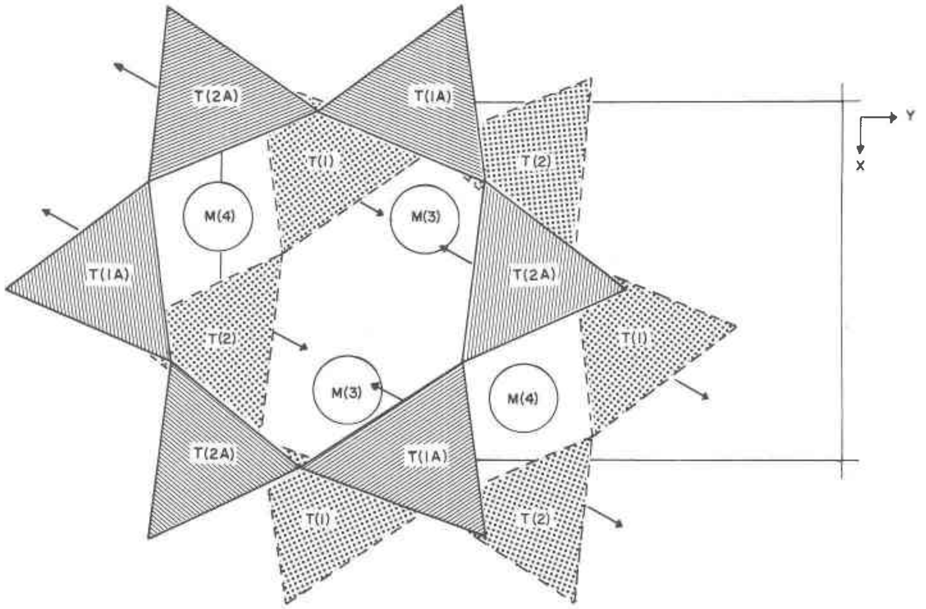

Fig. 2. Interlayer cations in relation to tetrahedral sheets above (lines) and below (dots). Directions of layer offset due to cation repulsion are shown by arrows.

triclinic angle α in a II*b*-4 chlorite, therefore, can be regarded as evidence for substantial ordering of a trivalent cation in the M(4) interlayer site. We have measured $\alpha = 90.43°$ for the ordered Kenya chlorite studied by Steinfink (1958). We would expect $\alpha = 90°$ only for disordered or incompletely ordered II*b*-4 chlorites, and we would regard such chlorites as less stable than the fully ordered specimens.

Conclusions

The one-dimensional projections and the three-dimensional refined structures show the Cr^{3+} to occur in octahedral interlayer coordination, in agreement with the findings of Bish (1977). For the II*b*-4 polytype it is evident from bond lengths and scattering factors that Cr^{3+}, Al, and Fe^{3+} concentrate in the M(4) site within the interlayer. We therefore conclude that Lapham's (1958) classification based on the structural location of Cr^{3+} is no longer applicable, and propose, as suggested previously by Bayliss (1975) and Bish (1977), that the names kotschubeite and kämmererite be dropped and that the prefix "chromian" be applied to the accepted Mg–Fe chlorite species nomenclature. According to the simplified nomenclature recommended by Bayliss, all ten chlorites in this study are chromian clinochlores because Mg is the dominant divalent cation.

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References

Bailey, S. W. and B. E. Brown (1962) Chlorite polytypism: I. Regular and semi-random one-layer structures. *Am. Mineral., 47,* 819–850.

Baur, W. H. (1978) Variation of mean Si–O bond lengths in silicon–oxygen tetrahedra. *Acta Crystallogr., B34,* 1751–1756.

Bayliss, P. (1975) Nomenclature of the trioctahedral chlorites. *Can. Mineral., 13,* 178–180.

Besnus, Y., G. Fusil, C. Janot, M. Pinta and G. Sieffermann (1976) Characteristics of some weathering products of chromitic ultrabasic rocks in Bahia State, Brazil: nontronites, chlorites and chromiferous talc. *Proc. Internat. Clay Conf., 1975,* 27–34.

Bish, D. L. (1977) A spectroscopic and X-ray study of the coordination of Cr^{3+} ions in chlorites. *Am. Mineral., 62,* 385–389.

Booth, A. D. (1948) *Fourier Technique in X-ray Organic Structure Analysis.* Cambridge University Press, Cambridge, England.

Brown, B. E. and S. W. Bailey (1963) Chlorite polytypism: II. Crystal structure of a one-layer Cr-chlorite. *Am. Mineral., 48,* 42–61.

Burns, R. G. (1970) *Mineralogical Applications of Crystal Field Theory.* Cambridge University Press, Cambridge, England.

Burns, V. M. and R. G. Burns (1975) Mineralogy of chromium. *Geochim. Cosmochim. Acta, 39,* 903–910.

Damodaran, K. T. and B. Somasekar (1976) Chrome chlorite (kotschubeite) from the Nuggihalli schist belt. *Clays Clay Minerals, 24,* 31–35.

Dollase, W. A. (1969) Crystal structure and cation ordering of piemontite. *Am. Mineral., 54,* 710–717.

Finger, L. W. and E. Prince (1975) *A System of Fortran IV Computer Programs* for *Crystal Structure Computations.* U. S. Department of Commerce, National Bureau of Standards Technical Note 854, Washington, D.C.

International Tables for X-Ray Crystallography, Vol. III (1962) C. H. MacGillavry and G. D. Rieck, Eds., Kynoch Press, Birmingham, England.

Lapham, D. M. (1958) Structural and chemical variations in chromium chlorite. *Am. Mineral., 43,* 921–956.

Lister, J. S. and S. W. Bailey (1967) Chlorite polytypism: IV. Regular two-layer structures. *Am. Mineral., 52,* 1614–1631.

McCormick, G. R. (1975) A chemical study of kämmererite, Day Book Body, Yancey County, North Carolina. *Am. Mineral., 60,* 924–927.

Neuhaus, A. (1960) Über die Ionenfarben der Kristalle und Minerale am Beispiel der Chromfärbungen. *Z. Kristallogr., 113,* 195–233.

Robinson, K., G. V. Gibbs and P. H. Ribbe (1971) Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science, 172,* 567–570.

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. (1958) The crystal structure of chlorite. II. A triclinic polymorph. *Acta Crystallogr., 11,* 195–198.

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