

## CRYSTAL STRUCTURE REFINEMENT AND MÖSSBAUER SPECTROSCOPY OF AN ORDERED, TRICLINIC CLINOCHLORE

JOSEPH R. SMYTH,<sup>1</sup> M. DARBY DYAR,<sup>2</sup> HOWARD M. MAY,<sup>3</sup> OWEN P. BRICKER<sup>4</sup> AND JAMES G. ACKER<sup>4</sup>

<sup>1</sup> Department of Geological Sciences, University of Colorado, Boulder, Colorado 80309-0250

<sup>2</sup> Department of Geology and Astronomy, West Chester University, West Chester, Pennsylvania 19383

<sup>3</sup> US Geological Survey, Water Resources Division, 3215 Marine Street, Boulder, Colorado 80303

<sup>4</sup> US Geological Survey, Reston, Virginia 22092

**Abstract**—The crystal structure of a natural, ordered *Iib-4* triclinic clinochlore has been refined in space group *C1* from 4282 unique X-ray intensity measurements of which 3833 are greater than 3 times the statistical counting error ( $3\sigma$ ). Unit cell parameters are  $a = 5.3262(6)$  Å;  $b = 9.226(1)$  Å;  $c = 14.334(3)$  Å;  $\alpha = 90.56(2)^\circ$ ;  $\beta = 97.47(2)^\circ$ ; and  $\gamma = 89.979(9)^\circ$ , which represents the greatest deviation from monoclinic symmetry yet recorded for a triclinic chlorite. The final weighted  $R$  is 0.059 for reflections with  $I > 3\sigma$  and 0.064 for all reflections. The chemical formula is  $(\text{Mg}_{0.996}\text{Fe}_{0.004})^{\text{M1}}(\text{Mg}_{0.962}\text{Fe}_{0.038})^{\text{M2}}_2(\text{Si}_{2.96}\text{Al}_{1.04})\text{O}_{10}(\text{OH})_2(\text{Mg}_{0.996}\text{Fe}_{0.004})^{\text{M3}}_2(\text{Al}_{0.841}\text{Fe}^{\text{III}}_{0.102}\text{Cr}_{0.004}\text{Ti}_{0.004})^{\text{M4}}(\text{OH})_6$ , which is consistent with electron microprobe (EMP), wet chemical analyses, Mössbauer spectroscopy and X-ray structure refinement. The high degree of ordering of the divalent versus trivalent octahedral cations in the interlayer is noteworthy, with  $\text{Fe}^{\text{III}}$  and Al in M4 and virtually no Fe in M3. In the 2:1 layer, M1 and M2 each contain similar amounts of Fe. The 2 tetrahedral sites have nearly identical mean oxygen distances and volumes, and thus show no evidence of long-range cation ordering.

**Key Words**—Cation Ordering, Chlorite, Clinochlore, Crystal Structure, Mössbauer.

### INTRODUCTION

Chlorite is a common to abundant mineral in low- to intermediate-grade metamorphosed mafic and ultramafic rocks. It is abundant in altered sea floor basalts and may provide a vehicle by which hydrogen (H) is subducted into the upper mantle. Inasmuch as H is a major flux for partial melting, the thermodynamic stability of chlorite is significant to models of subduction, dehydration and magma genesis. Chlorites are also important components of metamorphic terranes impacted by acidified atmospheric deposition in the eastern United States and Canada, and thus their weathering characteristics influence water chemistry and watershed response to acidic inputs. The thermodynamic parameters of chlorite are likely to be affected by various degrees of ordering of the octahedral and tetrahedral cations, so that rates of weathering for chlorites may be affected by cation occupancies of the various structural sites.

In this study, we characterize the composition and crystal structure of a natural clinochlore using X-ray diffraction (XRD), EMP, wet chemistry and Mössbauer spectroscopy, and examine octahedral and tetrahedral cation ordering. The XRD data are used to clarify the interpretation of Mössbauer results, and site assignments from both methods are compared. In this study, a large single-crystal sample approximately 4 by 8 cm in size from West Chester, Pennsylvania, was obtained from the Smithsonian Institution. The speci-

men, NMNH #R4513, was originally described by Clark and Schneider (1890), and is also being used in our ongoing study of chlorite weathering.

The structural chemistry of the chlorite group has been reviewed by Bailey (1988). The chlorite structure consists of a 2:1 layer with an octahedral sheet sandwiched between 2 tetrahedral sheets. The 2:1 layers alternate with brucite-like interlayers. The 2:1 layer has a chemical formula  $(\text{Mg,Fe})_3\text{Al}_{1+x}\text{Si}_{3-x}\text{O}_{10}(\text{OH})_2$  with a net charge of  $-(1+x)$  per formula unit. The interlayer has a formula of  $\text{Mg}_{2-x}(\text{Al,Fe,Cr})_{1+x}(\text{OH})_6$  with a net charge of  $+(1+x)$ . Although other polytypes are possible, the *Iib* polytype is the most common and exists with monoclinic (*C2/m*) and triclinic (*C1*) modifications. The site nomenclature is the same for both modifications. The tetrahedral sheets are each composed of equal numbers of 2 distinct tetrahedra, T1 and T2. The octahedral sheet in the 2:1 layer comprises 2 distinct octahedral sites, M1 and M2, with M1 at the origin, *trans*-bonded to OH, and M2 in a general position, *cis*-bonded to OH. Similarly, the interlayer comprises 2 distinct octahedra, M3 and M4, with M3 in a general position and M4 on an inversion, so that there are half as many M4 as M3 sites per layer.

Previous XRD studies (Phillips et al. 1980; Rule and Bailey 1989; Zheng and Bailey 1989; Joswig et al. 1980, 1989; Nelson and Guggenheim 1993) indicate little if any ordering of Al and Si between T1 and T2, the sites being nearly identical in volume and average T-O distance. MAS NMR studies of both <sup>27</sup>Al and <sup>29</sup>Si,

Table 1. Mössbauer peak assignments.

Assignment	Average $\delta$ , or isomer shift (mm/s)	Average $\Delta$ , or quadrupole splitting (mm/s)
Fe <sup>II</sup> <i>cis</i> -M2	1.09 ± 0.03	2.59 ± 0.09
Fe <sup>II</sup> <i>trans</i> -M1	1.11 ± 0.02	2.33 ± 0.08
Fe <sup>II</sup> "hydroxide"	1.14 ± 0.04	2.66 ± 0.07
Fe <sup>III</sup> tet	0.12	0.39 ± 0.09
Fe <sup>III</sup> <i>cis</i> -M3	0.35	0.40
Fe <sup>III</sup> <i>trans</i> -M4	0.33	0.65

however (Welch et al. 1995), indicate considerable short-range order and Al-O-Al avoidance in the tetrahedral sheet, even for synthesized samples, although significant ordering based on the crystallographic distinction between the tetrahedral sites has not been documented.

The XRD studies indicate considerable ordering of octahedral cations. The 2 octahedra in the interlayer differ considerably in volume, distortion and mean cation-oxygen distance. Trivalent cations (Al, Cr and Fe(III)) concentrate in the interlayer, creating a net positive charge to balance the net negative charge on the 2:1 layer. Further, trivalent cations tend to concentrate into the smaller M4 site. If the cations are disordered over the 2 sites, the symmetry can be monoclinic, whereas ordering of trivalent cations into M4 causes a difference ( $D$ ) in the mean cation oxygen dis-

Table 2. Chemical composition determined by electron microprobe and wet chemistry for *IIB-4* clinocllore.

Oxide	Wt%	Cation	per 18 Oxygens
SiO <sub>2</sub>	31.68	Si	2.957
TiO <sub>2</sub>	0.05	Ti	0.004
Al <sub>2</sub> O <sub>3</sub>	17.13	<sup>IV</sup> Al	1.043
		<sup>VI</sup> Al	0.841
Cr <sub>2</sub> O <sub>3</sub>	0.05	Cr	0.004
Fe <sub>2</sub> O <sub>3</sub>	1.34	Fe <sup>III</sup>	0.094
FeO	1.62	Fe <sup>II</sup>	0.126
MgO	34.76	Mg	4.836
MnO	0.08	Mn	0.006
CaO	0.00	Ca	0.000
H <sub>2</sub> O <sup>†</sup>	13.24	H	8.274
Total	100.0		

<sup>†</sup> By difference.

tances of the 2 sites that strongly correlates with the deviation of  $\alpha$  from 90°. Evidence for ordering of Fe and Mg in the octahedral sheet of the 2:1 layer is less clear.

Mössbauer studies have not succeeded in determining site assignments of Fe due to confusion in the literature regarding the appropriate number and assignment of spectra doublets. Because Fe atoms can occupy any of the octahedrally coordinated sites in the structure, this variability leads to a potential for 4 doublets corresponding to each oxidation state of Fe in

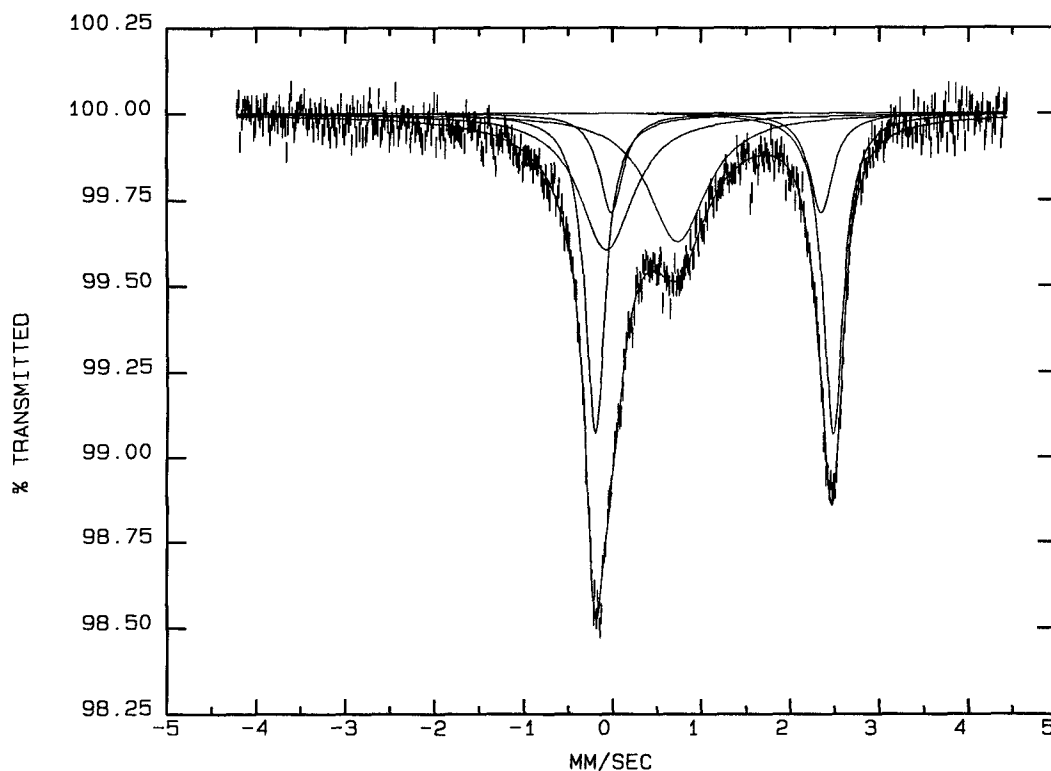


Figure 1. Mössbauer spectrum of the West Chester, Pennsylvania, clinocllore.

Table 3. Results of fit to Mössbauer spectrum.

Oxide	Isomer shift	Quadropole splitting	% of total Fe	Atoms pfu
Fe <sup>III</sup> in M4	0.33	0.80	46.0	0.102
Fe <sup>II</sup> in M1	1.16	2.37	14.5	0.032
Fe <sup>II</sup> in M2	1.13	2.68	39.5	0.087

each spectrum. Most Mössbauer studies report only 1 or 2 Fe(II) doublets (Taylor et al. 1968; Coey 1975; Ericsson et al. 1977; Goodman and Bain 1978; Blaauw et al. 1980; Borggaard et al. 1982; Kodama et al. 1982; Ballet et al. 1985; Raclavská and Raclavský 1988; Aramu et al. 1989; Christofides et al. 1994) that are generally assigned to the M1 and M2 sites, but are recognized to be potentially indistinguishable from M3 and M4 doublets. In many of these studies (for example, Christofides et al. 1994), the authors were primarily interested in Fe(III)/Fe(II) ratios, and so did not pursue more elaborate fitting schemes to determine Fe occupancy of the interlayer sites. A recent study by Gregori and Mercader (1994) fit 4 doublets to the Mössbauer spectra of some Argentine chlorites; however, their site assignments suggested Fe(II) in M1, M2 and tetrahedral coordination, with Fe(III) assigned to the interlayer. Four recent studies have modeled both interlayer and octahedral site occupancy of Fe(II) in the Mössbauer spectra of chlorite (Townsend et al. 1986; DeGrave et al. 1987; de Parseval et al. 1991; Pal et al. 1992). Their collective assignments of the Mössbauer doublets in chlorite spectra are used in this study (Table 1).

Note that the parameters for Fe(II) *cis*-M2 and Fe(II) "hydroxide" are very similar, with the quad-

ruple splitting of the Fe(II) "hydroxide" doublet being only slightly higher than that for Fe(II) *cis*-M2; this may well have contributed to past confusion. Only when both doublets are fit to the same spectrum can their distinct contributions be recognized. This makes it almost impossible (without independent data from other techniques) to determine accurate Fe(II) site occupancies in samples where Fe(II) is ordered in either Fe(II) *cis*-M2 or Fe(II) "hydroxide", but not in both. We have therefore undertaken a combined study using both X-ray single-crystal diffraction and Mössbauer spectroscopy to constrain site assignments and cation ordering in clinocllore.

### CHEMICAL ANALYSIS

An average of 10 spot analyses were obtained by EMP and gave an Fe content of 2.81 wt% with Fe as FeO. Fe contents were variable, ranging from 2.6 to 3.2 wt% FeO. Small (typically <10 μm in size) opaque inclusions are also visible in the optical microscope. These are sporadically distributed, with some areas free of inclusions. The average chemical analysis is given in Table 2, with ferrous-ferric ratios determined from Mössbauer spectroscopy and by wet chemical analysis. H<sub>2</sub>O content was determined by difference of the oxide total from 100%. The calculated H content is 8.2 atoms per formula unit, in good agreement with the ideal composition of 8.0. The total of other cations in the formula unit is 9.911, which suggests minor cation vacancy in the structure.

The Fe(II)/Fe(III) ratio was determined by wet chemical methods using a colorimetric method (Stucki 1981; Stucki and Anderson 1981; Komadel and Stucki 1988) involving an organic chromophore during the

Table 4. Final positional and thermal parameters for clinocllore from RFINE.

Atom	x	y	z	Occ.	B <sub>eq</sub>	β <sub>11</sub>	β <sub>22</sub>
Talc layer							
M1	0.0	0.0	0.0	Mg <sub>0.996</sub> Fe <sub>0.034(6)</sub>	0.72(5)	0.0038(5)	0.0014(2)
M2	0.0016(2)	0.3339(1)	-0.00002(8)	Mg <sub>0.962</sub> Fe <sub>0.038(4)</sub>	0.72(4)	0.0041(4)	0.0015(1)
T1	0.2332(2)	0.1696(1)	0.19249(7)	Si <sub>1.0,75</sub> Al <sub>0.25</sub>	0.85(3)	0.0044(3)	0.0016(1)
T2	0.7339(2)	0.0028(1)	0.19262(7)	Si <sub>1.0,75</sub> Al <sub>0.25</sub>	0.87(4)	0.0043(3)	0.0016(1)
O1	0.1937(4)	0.1682(2)	0.0770(2)	O <sub>1.0</sub>	0.98(9)	0.0038(7)	0.0015(2)
O2	0.6936(4)	0.0013(2)	0.0770(2)	O <sub>1.0</sub>	0.96(9)	0.0046(7)	0.0016(2)
O3	0.2070(5)	0.3372(3)	0.2350(2)	O <sub>1.0</sub>	1.7(2)	0.016(1)	0.0032(3)
O4	0.5192(5)	0.1070(3)	0.2346(2)	O <sub>1.0</sub>	1.6(1)	0.0130(9)	0.0037(3)
O5	0.0198(5)	0.0672(3)	0.2339(2)	O <sub>1.0</sub>	1.6(1)	0.0127(9)	0.0037(3)
OH1	0.6922(4)	0.3341(3)	0.0732(2)	O <sub>1.0</sub>	1.0(1)	0.0064(8)	0.0026(3)
H1	0.721(8)	0.336(5)	0.181(4)	H <sub>1.0</sub>	1.7(9)		
Brucite layer							
M3	-0.0004(2)	0.1667(1)	0.5001(1)	Mg <sub>0.996</sub> Fe <sub>0.004(4)</sub>	0.91(5)	0.0061(4)	0.0015(1)
M4	0.0	0.5	0.5	Al <sub>0.833</sub> Fe <sub>0.102(6)</sub>	0.77(6)	0.0047(5)	0.0013(2)
OH2	0.1644(5)	-0.0012(3)	0.4304(2)	O <sub>1.0</sub>	1.2(1)	0.0092(8)	0.0025(3)
OH3	0.1315(5)	0.3427(3)	0.4304(2)	O <sub>1.0</sub>	1.2(1)	0.0099(8)	0.0027(3)
OH4	0.6318(5)	0.1542(3)	0.4311(2)	O <sub>1.0</sub>	1.1(1)	0.0092(8)	0.0028(3)
H2	0.12(2)	0.001(9)	0.373(6)	H <sub>1.0</sub>	4.(1)		
H3	0.08(1)	0.323(7)	0.379(5)	H <sub>1.0</sub>	4.(1)		
H4	0.58(1)	0.143(5)	0.363(4)	H <sub>1.0</sub>	4.(1)		

sample digestion. Both Fe(II) and total Fe are obtained from a single dissolution. This method gave a total Fe content of 2.59 wt% as FeO with 57.4% of this as Fe(II), and 42.6% as Fe(III). Errors are estimated at less than  $\pm 5\%$  absolute. The total Fe content obtained by this method is thus slightly lower than the average of those obtained by EMP.

### MÖSSBAUER SPECTROSCOPY

Samples were mounted with the ideal thickness of 5.22 mg Fe/cm<sup>2</sup> of sample/mount in the holder, using the method of Long et al. (1984) for high background conditions. A source of 50–20 mCi <sup>57</sup>Co in Pd was used on an Austin Science Associates constant acceleration spectrometer. Results were calibrated against an  $\alpha$ -Fe foil of 6  $\mu$ m thickness and 99% purity. Spectra were folded at a channel number selected using auto-correction to ensure a proper match of peak positions after folding. Spectra were fitted using a version of the program STONE. The program uses a nonlinear regression procedure with the ability to constrain any set of parameters or linear combination of parameters. Lorentzian line shapes were used for resolving peaks. Peak-fitting procedures in general followed those described in Dyar (1990), with modifications described in Grant (1995). A statistical best fit was obtained for each model per spectrum using the  $\chi^2$  and/or misfit parameters, as described in Dyar (1984).

A typical spectrum is given in Figure 1. The observed peak areas give occupancies of  $0.032 \pm 0.002$  atoms of Fe(II) in M1 and  $0.087 \pm 0.002$  atoms of Fe(II) in M2 (Table 3), propagating the  $\pm 1\%$  absolute error on peak areas. These results indicate significant ordering of Fe(II) in M2 and are in very close agree-

ment with site assignments determined by XRD (below). Fits with greater than 3 doublets were attempted (that is, with Fe(II) modeled in M1, M2 and "hydroxide" sites) and rejected because they did not converge without heavy peak constraints. Fits with multiple Fe(III) doublets were also attempted and would not converge, even with heavy constraints. Peak assignments are based on previous work cited and on Fe occupancy refinements from X-ray data as described below. Fe(III)/Fe(II) ratios determined from Mössbauer spectroscopy are consistent with the wet chemical analyses. Absolute errors are estimated at  $\pm 1\%$  for doublet areas (that is, for Fe in each individual site and valence state), and  $\pm 0.02$  mm/s for isomer shift and quadrupole splitting, based on similar spectra by Grant (1995).

### X-RAY DIFFRACTION

#### Cell Refinement

A clear, transparent cleavage fragment approximately  $300 \times 600 \times 100 \mu\text{m}$  was cut from a larger cleavage flake with scissors. The fragment was mounted in acetone-soluble cement and the edges trimmed by grinding on a glass plate to about  $150 \times 300 \times 100 \mu\text{m}$ . The fragment was mounted on a Siemens P4 automated single-crystal diffractometer on an Mo-target rotating anode X-ray generator with a vertical graphite crystal monochromator. The diffractometer and monochromator were aligned using a ruby crystal with cell parameters known to 1 part in 100,000. Ruby cell parameters were reproduced to within 1 part in 40,000 of the known values.

Initial orientation was determined by means of a rotation photograph from which 15 peaks were indexed using an automatic indexing routine. After application of an appropriate transformation matrix, a unit cell consistent with  $C1$  or  $C\bar{1}$  (triclinic) was obtained. The cell was refined from centered angles of 24 strong reflections with  $9^\circ < 2\theta < 35^\circ$  centered in both positive and negative  $2\theta$  positions. The average peak widths were about  $1.5^\circ 2\theta$ . The refined cell parameters are  $a = 5.3262(6) \text{ \AA}$ ;  $b = 9.226(1) \text{ \AA}$ ;  $c = 14.334(3) \text{ \AA}$ ;  $\alpha = 90.56(2)^\circ$ ;  $\beta = 97.47(2)^\circ$ ; and  $\gamma = 89.979(9)^\circ$ . The basal spacing computed from these values is  $d(001) = 14.212(4) \text{ \AA}$ . The cell parameters are consistent with polytype *I1b-4* (triclinic).

#### Intensity Data

A set of X-ray intensity data covering a hemisphere with  $3^\circ < 2\theta < 60^\circ$  was measured using a variable scan rate, constant precision method with scan rates varying from 8 to  $30^\circ 2\theta$  per minute. The X-ray generator was operating at 50 kV and 200 mA. This gave 4793 intensity measurements, of which 4282 were unique, and 3833 of these were greater than  $3\sigma$ . Data were corrected for Lorentz and polarization effects.

Table 4. Extended.

$\beta_{23}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
0.0018(1)	0.0013(2)	0.0011(2)	0.0005(1)
0.0018(1)	0.0011(1)	0.0012(1)	0.0005(1)
0.0020(1)	0.0009(1)	0.0012(1)	0.0003(1)
0.0021(1)	0.0008(1)	0.0012(1)	0.0006(1)
0.0025(1)	0.0013(3)	0.0012(3)	0.0006(1)
0.0024(1)	0.0012(3)	0.0012(3)	0.0007(1)
0.0025(1)	0.0004(4)	0.0017(3)	0.0006(2)
0.0024(1)	0.0019(4)	0.0018(3)	0.0004(2)
0.0025(1)	-0.0002(4)	0.0015(3)	0.0009(2)
0.0020(1)	0.0014(4)	0.0015(3)	0.0006(2)
0.0021(1)	0.0007(2)	0.0015(1)	0.0005(1)
0.0017(1)	0.0004(2)	0.0012(1)	0.0005(1)
0.0021(1)	0.0007(4)	0.0014(3)	0.0006(2)
0.0019(1)	0.0006(4)	0.0016(3)	0.0004(2)
0.0018(1)	0.0011(4)	0.0015(3)	0.0003(2)

Table 5. Cation oxygen distances and coordination polyhedral volumes and distortions for ordered *Ilb-4* clinochlore.

Atoms	Distance	Atoms	Distance
<b>2:1 LAYER</b>			
<b>Tetrahedra</b>			
T(1)-O(1)	1.641(4)	T(2)-O(4)	1.662(4)
O(3)	1.669(3)	O(2)	1.643(4)
O(4)	1.669(3)	O(3)	1.663(4)
O(5)	1.650(4)	O(5)	1.668(4)
<T(1)-O>	1.657	<T(2)-O>	1.659
Volume (Å <sup>3</sup> )	2.334		2.340
T.Q.E.	1.0007		1.0006
A.V.	3.25		3.04
<b>Octahedra</b>			
M(1)-OH(1)	2.060(3)	M(2)-OH(1)	2.064(3)
OH(1)	2.060(3)	O(1)	2.084(3)
O(1)	2.089(3)	OH(1)	2.066(4)
O(1)	2.089(3)	O(1)	2.078(4)
O(2)	2.086(3)	O(2)	2.079(3)
O(2)	2.086(3)	O(2)	2.084(3)
<M(1)-O>	2.078	<M(2)-O>	2.076
Volume (Å <sup>3</sup> )	11.779		11.741
O.Q.E.	1.0105		1.0103
A.V.	34.49		34.05
<b>INTERLAYER</b>			
M(3)-OH(2)	2.089(4)	M(4)-OH(3)	1.935(4)
OH(2)	2.084(4)	OH(4)	1.923(4)
OH(3)	2.084(4)	OH(2)	1.930(3)
OH(3)	2.086(4)	OH(2)	1.930(3)
OH(4)	2.079(4)	OH(3)	1.935(4)
OH(4)	2.083(4)	OH(4)	1.924(4)
<M(3)-O>	2.084	<M(4)-O>	1.929
Volume (Å <sup>3</sup> )	11.483		9.398
O.Q.E.	1.0344		1.0129
A.V.	106.70		42.38
H(1)-OH(1)	1.15(8)	H(2)-OH(2)	1.03(9)
		O5	1.87(8)
H(3)-OH(3)	0.99(7)	H(4)-OH(4)	0.98(6)
O(3)	1.95(7)	O(4)	1.85(6)

Key: T.Q.E. = tetrahedral quadratic elongation; A.V. = angle variance; O.Q.E. = octahedral quadratic elongation.

Data were corrected for absorption using an analytical absorption correction routine based on the measured distance from the crystal center to bounding *hkl* faces to determine size and shape of the crystal.

### Structure Refinement

Starting with atomic position parameters of Joswig et al. (1980) and isotropic temperature factors, the *R* reduced to 0.085 after 5 cycles of refinement. Using scattering factors for fully ionized cations and O<sup>-1</sup> in the refinement program RFINE (Finger and Prince 1975), the Fe and Mg occupancies of the octahedral sites were refined so that total Fe occupancy was constrained to that of the microprobe chemical analysis (Table 2). The occupancy of M3 refined to 0.996(4) Mg and M4 to 0.918(5) Al (+Mg) and 0.082 Fe. The occupancy of M1 refined to 0.040(5) Fe and M2 to 0.048 Fe, with all sites constrained to full total occu-

pancy. This model gave an anomalously small equivalent isotropic atomic displacement parameter of 0.45 for M4. Also, the total amounts of Al and Mg are somewhat larger than indicated by microprobe chemical analysis.

The chemical analysis indicates a small deficiency in octahedral cations. The X-ray structure refinement method determines the number of electrons at a given site, so octahedral vacancies cannot be uniquely determined. The X-ray results thus indicate that the number of electrons in the octahedral sites decreases as M4(#e<sup>-</sup>) > M2(#e<sup>-</sup>) = M1(#e<sup>-</sup>) > M3(#e<sup>-</sup>). If all trivalent cations (except tetrahedral Al), plus the trace Ti, are arbitrarily assigned to M4, the smallest of the octahedral sites, the total occupancy at this site is 0.95. Incorporating this 5% vacancy at M4 into the model, and refining occupancies with constraints otherwise as above, yields a model that is consistent with the Mössbauer spectroscopy and wet chemical analyses, and within the range of Fe contents observed by electron microprobe. This model gives Fe occupancies of 0.034(6) for M1, 0.038(4) for M2, 0.004(4) for M3 and 0.110(6) (= 0.102Fe<sup>III</sup> + 0.004Cr + 0.004 Ti) for M4. The remaining light cation (Al or Mg) at M4 agrees with the amount of octahedral Al (Table 2). Also, the equivalent isotropic atomic displacement parameter (*B* = 0.77 Å<sup>2</sup>) is consistent with those of the other M sites. The amount of Fe at this site is thus consistent with total Fe(III) determined by both wet chemical analysis and Mössbauer spectroscopy. This gives the formula of (Mg<sub>0.966</sub>Fe<sub>0.034</sub>)<sup>M1</sup>(Mg<sub>0.962</sub>Fe<sub>0.038</sub>)<sup>M2</sup><sub>2</sub>(Si<sub>2.96</sub>Al<sub>1.04</sub>)O<sub>10</sub>(OH)<sub>2</sub>(Mg<sub>0.996</sub>Fe<sub>0.004</sub>)<sup>M3</sup><sub>2</sub>(Al<sub>0.841</sub>Fe<sup>III</sup><sub>0.102</sub>Cr<sub>0.004</sub>Ti<sub>0.004</sub>)<sup>M4</sup>(OH)<sub>6</sub>, which contains slightly more total Mg atoms (4.88) than indicated by electron microprobe (4.84), but is within the analytical error of the probe.

Finally, H atoms were located and refined using isotropic displacement factors. The positions of H atoms in the interlayer were refined without constraint. However, the H1 position drifted to a position that gave an unreasonably long O-H distance and large displacement parameter. The *z* coordinate of this H was constrained to that of a significant maximum in the difference Fourier while *x*, *y* and *B* were refined without constraint. The final weighted *R* (*R*<sub>w</sub>) for the refinement reduced to 0.059 for reflections greater than 3σ, and 0.064 for all reflections. Final position and temperature factors are given in Table 4. Selected nearest neighbor oxygen distances and coordination polyhedral volumes and distortions are given in Table 5.

### DISCUSSION

The atom positions, cell parameters and nearest neighbor cation-anion distances are similar to those found by Joswig and Feuss (1989) and Zheng and Bailey (1989). The nearly identical mean T-O distances, tetrahedral volumes and scattering efficiencies for the

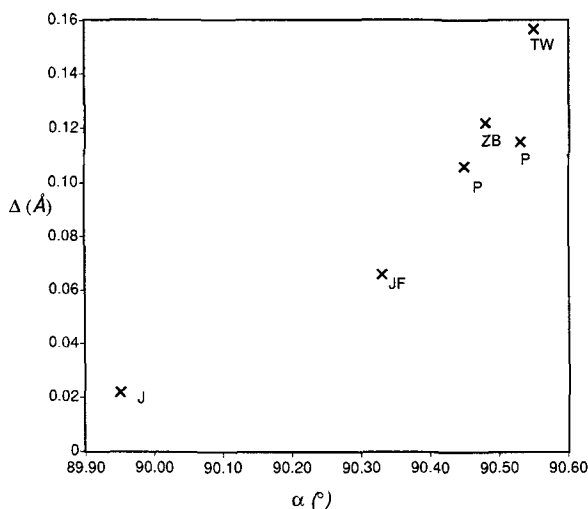


Figure 2. Plot of the difference in mean cation-oxygen distance for the M3 and M4 octahedra of the interlayer ( $\Delta$ ) versus the  $\alpha$  cell parameter for //b chlorites. This plot shows increasing deviation from monoclinic symmetry with increasing cation order in the interlayer. Data are from Joswig et al. (1980) (J), Phillips et al. (1980) (P), Joswig and Feuss (1989) (JF), Zheng and Bailey (1989) (ZB) and this work (TW).

T1 and T2 tetrahedra indicate complete disorder of Al and Si over these sites. Welch et al. (1995) reported NMR spectra of  $^{27}\text{Al}$  and  $^{29}\text{Si}$  that indicate considerable short-range order and Al-O-Al avoidance in 2 synthetic clinocllore samples. The current results are consistent with those of Welch et al. (1995), but there is no tendency for long-range ordering of Al into 1 of the 2 tetrahedral sites.

Nearly identical values of polyhedral volume and mean M-O distance for the M1 and M2 octahedra of the 2:1 layer indicate similar Fe and Mg occupancies. The X-ray refinement using scattering factors from ionized cations (Cromer and Mann 1968) indicates 3.4% occupancy of M1 and 3.8% occupancy of M2 by Fe, for a total of 0.110 cations of Fe per formula unit in these 2 sites. The scattering intensities and volumes of these 2 sites are identical within error indicating no tendency for Fe ordering between them. Both Mössbauer spectroscopy and X-ray diffraction thus indicate no preference of Fe(II) for M2. Also, M1 and M2 are nearly identical in volume, distortion and mean nearest neighbor distances. Based on the observed occupancies and multiplicities of the 2 sites, we assign the Mössbauer peak with  $\delta = 1.16$  mm/s and  $\Delta = 2.365$  mm/s to Fe(II) in M1, and that with  $\delta = 1.134$  mm/s and  $\Delta = 2.681$  to Fe(II) in M2. The observed peak areas then give occupancies of 3.2% Fe(II) in M1 and 4.3% Fe(II) in M2 (Table 3), in very close agreement with those determined by X-ray. The latter assignment can be made with confidence because corroborating XRD results argue against its being interpreted as Fe(II) in M3 or M4.

We then assign the remaining Mössbauer doublet with  $\delta = 0.328$  mm/s and  $\Delta = 0.80$  mm/s to Fe(III) at M4. This gives an Fe(III) occupancy of 10.2% in M4 in very close agreement with the 10.1% Fe occupancy determined by XRD. This X-ray result is, of course, dependent on our assignment of 5% vacancy to this site. This assignment is not entirely arbitrary. Without the vacancy, the Fe occupancy of M4 refined to 8.2%, but this model gave a somewhat anomalously small atomic displacement parameter. This anomaly is avoided and essentially complete agreement between chemical analysis, Mössbauer spectroscopy and XRD is obtained by assignment of 5% vacancy to this site.

The anisotropic atomic displacement factors observed in this X-ray refinement are somewhat anomalous in being strongly prolate parallel to  $c$ , particularly for M1, M2, M3, M4, T1, T2, O1, O2 and OH1, but much less strongly for the remaining O and OH positions. This has been observed by many previous authors in phyllosilicate refinements (for example, Zheng and Bailey 1989) and ascribed to possible error in absorption correction. This is a possible explanation, but several different arbitrary crystal shapes were used for the absorption correction, and the effect persisted.

The natural clinocllore sample studied here thus shows a high degree of cation order in the interlayer, as evidenced by the difference between the mean M4-OH (1.922(4) Å) and M3-OH (2.083(4) Å) distances,  $\Delta$ , which is equal to 0.157 Å. Phillips et al. (1980) noted a correlation between the  $\alpha$  cell parameter and cation ordering in the interlayer that was discussed further by Joswig and Feuss (1989). Based on high-precision single-crystal refinement, the results of our analysis show the largest  $\alpha$  value (90.56°) and the largest  $\Delta$  yet reported for //b-4 chlorites. These parameters are plotted in Figure 2, which shows a strong correlation and is consistent with the high degree of trivalent cation ordering in the current sample. The only sample that falls slightly from the smooth trend is one of the high Cr samples described by Phillips et al. (1980). The strong correlation indicates that the degree of cation order may be inferred from cell parameters that are readily refined to high precision by Rietveld methods from powder data (Walker and Bish 1992).

#### ACKNOWLEDGMENTS

This work was supported by US Department of Energy Office of Basic Energy Sciences under grant DE-FG02-92ER14233 to the University of Colorado, and by the US Geological Survey. Manuscript preparation was supported by National Science Foundation Grant EAR-9526916. The authors thank J. Drexler at the University of Colorado for EMP analyses, and J. Stucki at the University of Illinois for wet chemical analyses. The authors thank S. Guggenheim at the University of Illinois and an anonymous referee for helpful and constructive reviews. Use of trade names is only for pur-

poses of identification and does not imply endorsement by the US Geological Survey.

## REFERENCES

- Aramu F, Maxia F, Delunas A. 1989. Mössbauer spectroscopy of talc minerals. *Il Nuovo Cimento* 11(6):891–896.
- Bailey SW. 1988. Chlorites: Structures and crystal chemistry. *Rev Mineral* 19:347–398.
- Ballet O, Coey JMD, Burke KJ. 1985. Magnetic properties of sheet silicates; 2:1:1 layer minerals. *Phys Chem Miner* 12:370–378.
- Blaauw C, Stroink G, Leiper W. 1980. Mössbauer analysis of talc and chlorite. *J de Phys, Colloque* 41:C1-411–412.
- Borggaard OK, Lindgreen HB, Mørup S. 1982. Oxidation and reduction of structural iron in chlorite at 480°C. *Clays Clay Miner* 30:353–364.
- Christofides G, Thimiatis G, Koroneos A, Sklavounos S, Eleftheriadis G. 1994. Mineralogy and chemistry of Cr-chlorites associated with chromites from Vavdos and Vasilika ophiolite complexes (Chalkidiki, Macedonia, N. Greece). *Chemie der Erde, Geochem* 54:151–166.
- Clark FW, Schneider EA. 1890. Experiments upon the constitution of the natural silicates. *Am J Sci* 40:406–415.
- Coey JMD. 1975. The clay minerals: Use of the Mössbauer effect to characterize them and study their transformation. In: Hryniewicz AZ, Sawicki JA, editors. *Proc Int Conf Mössbauer Spectroscopy*, vol. 2. Krakow: Akademia Gorniczko-Hutnicza. p 333–354.
- Cromer DT, Mann J. 1968. X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr A* 24:321–324.
- DeGrave E, Vandenbruwaene J, Van Bockstael M. 1987.  $^{57}\text{Fe}$  Mössbauer spectroscopic analysis of chlorite. *Phys Chem Miner* 15:173–180.
- de Parseval P, Fournes L, Fortune J-P, Moine B, Ferret J. 1991. Distribution du fer dans les chlorites par spectrométrie Mössbauer ( $^{57}\text{Fe}$ ):  $\text{Fe}^{3+}$  Dans les chlorites du gisement de talc-chlorite de Trimouns (Pyrénées, France). *Acad Sci Paris* 312(II):1321–1326.
- Dyar MD. 1984. Precision and interlaboratory reproducibility of measurements of the Mössbauer effect in minerals. *Am Mineral* 69:1127–1144.
- Dyar MD. 1990. Mössbauer spectra of biotite from metapelites. *Am Mineral* 75:656–666.
- Ericsson T, Waeppling R, Punkivi K. 1977. Mössbauer spectroscopy applied to clay and related minerals. *Geologiska Föreningens i Stockholm Förhandlingar* 99:229–244.
- Finger LW, Prince E. 1975. A system of FORTRAN IV computer programs for crystal structure computations. *Nat Bur Standards Technical Note* 854. 128 p.
- Goodman BA, Bain DC. 1978. Mössbauer spectra of chlorites and their decomposition products. *Proc Int Clay Conf* 1978; Oxford. Amsterdam: Elsevier. p 65–74.
- Grant CA. 1995. Sources of experimental and analytical error in measurements of the Mössbauer effect in amphibole [Ph.D. thesis]. Eugene, OR: Univ of Oregon. 213 p.
- Gregori DA, Mercader RC. 1994. Mössbauer study of some Argentinean chlorites. *Hyperfine Interact* 83:495–498.
- Joswig W, Feuss H. 1989. Refinement of a one-layer triclinic chlorite. *Clays Clay Miner* 38:216–218.
- Joswig W, Feuss H, Mason SA. 1989. Neutron diffraction study of a one-layer monoclinic chlorite. *Clays Clay Miner* 37:511–514.
- Joswig W, Feuss H, Rothbauer R, Takeuchi Y, Mason SA. 1980. A neutron diffraction study of a one-layer triclinic chlorite (penninite). *Am Mineral* 65:349–352.
- Kodama H, Longworth G, Townsend MG. 1982. A Mössbauer investigation of some chlorites and their oxidation products. *Can Mineral* 20:585–592.
- Komadel P, Stucki JW. 1988. The quantitative assay of minerals for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  using 1,10-phenanthroline: III. A rapid photochemical method. *Clays Clay Miner* 36:379–381.
- Long GJ, Cranshaw TE, Longworth G. 1984. The ideal Mössbauer absorber thickness. *Mössbauer Effect Reference and Data J* 6:42–49.
- Nelson DO, Guggenheim S. 1993. Inferred limitations to the oxidation of Fe in chlorite: A high temperature single-crystal X-ray study. *Am Mineral* 78:1197–1207.
- Pal T, Dipankar D, Mitra S. 1992.  $^{57}\text{Fe}$  Mössbauer investigation of naturally oxidized chlorite. *Hyperfine Interact* 73:313–321.
- Phillips TL, Loveless JK, Bailey SW. 1980.  $\text{Cr}^{3+}$  coordination in chlorites: A structural study of ten chromian chlorites. *Am Mineral* 65:112–122.
- Raclavská H, Raclavský K. 1988. Chlorites of the Desná Unit, Hrubý Jeseník Mountains. 10th Conf Clay Mineral Petrol; Ostrava. p 113–118.
- Rule AC, Bailey SW. 1989. Refinement of the crystal structure of a monoclinic ferroan clinochlore. *Clays Clay Miner* 35:129–138.
- Stucki JW. 1981. The quantitative assay of minerals for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  using 1,10-phenanthroline: II. A photochemical method. *Soil Sci Soc Am J* 45:638–641.
- Stucki JW, Anderson WL. 1981. The quantitative assay of minerals for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  using 1,10-phenanthroline: I. Sources of variability. *Soil Sci Soc Am J* 45:633–637.
- Taylor GL, Ruotsala AP, Keeling RO Jr. 1968. Analysis of iron in layer silicates by Mössbauer spectroscopy. *Clays Clay Miner* 16:381–391.
- Townsend MG, Longworth G, Kodama H. 1986. Magnetic interaction at low temperature in chlorite and its products of oxidation: A Mössbauer investigation. *Can Mineral* 24:105–115.
- Walker JR, Bish DL. 1992. Application of Rietveld refinement techniques to a disordered I1b Mg-chamosite. *Clays Clay Miner* 40:319–322.
- Welch MD, Barras J, Klinowski J. 1995. A multinuclear NMR study of clinochlore. *Am Mineral* 80:441–447.
- Zheng H, Bailey SW. 1989. Structures of intergrown triclinic and monoclinic I1b chlorites from Kenya. *Clays Clay Miner* 37:308–318.

(Received 28 March 1996; accepted 15 September 1996; Ms. 2757)