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The Crystal Structure of Chlorite. I. A Monoclinic Polymorph*

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Detailed analysis of the crystal structure of an iron-rich monoclinic chlorite shows that it belongs in space group $C2$. The Si–O tetrahedra show a distinct rotation about an axis through the apex and perpendicular to the plane of the basal oxygens. It is found that the isomorphous replacement of magnesium and silicon in the octahedral and tetrahedral sites respectively is restricted to fixed positions in the structure. The hydroxyls of the brucite layer form a hydrogen bond with the basal oxygens of the talc layer which is 2·92 Å long. It is shown that the net negative charge on the talc layer in the unoxidized sample arises from replacement of silicon by aluminum in the tetrahedral sites, which is neutralized by excess positive charge on the brucite sheet.

Introduction

The chlorite minerals are formed by the alternate stacking of mica- or talc-type units of composition $A_{2-3}B_4O_{10}(OH)_2$, where A is usually Mg, Al, Fe, and B is Si and Al, followed by brucite-type layers of composition $A_{2-3}(OH)_6$. The sequence of atomic layers was first correctly deduced by Pauling (1930) from the ($00l$) intensity data which he obtained from single crystals of penninite and clinochlore. An attempt at a more detailed explanation of the chlorite structures was undertaken by McMurchy (1934), using powder diffraction methods. He confirmed Pauling's atomic parameters along the c axis of the unit cell and he was also able to arrive at a reasonable structure in the other two dimensions. However, a large amount of uncertainty still remained since the powder diffraction data provided no spectra with $k \neq 3n$, so that y parameters other than those which repeat at intervals of $\frac{1}{3}b$ could not be uniquely determined. Thus in the final structure, even though it provided a reasonable model, many atomic coordinates were subject to large uncertainties.

The next detailed investigation of these minerals was carried out by Brindley, Oughton & Robinson (1950). They employed single crystals of well ordered penninite in which the diffraction maxima with $k \neq 3n$ appeared as sharp spots. This allowed them to discover several polymorphic forms, although only two, a monoclinic and a triclinic variety, appear to be commonly encountered. If the discussion is restricted to the two polymorphs mentioned above, which have a unit cell approximately 14 Å high, then there can be only one mica-type and one brucite-type layer in this unit cell. These authors then show that the polymorphism must be caused by variations in stacking of the two Si–O networks relative to each other within the individual mica-type layer. Fig. 2 of their paper illustrates the possible Si–O stacking sequences, which are designated L, M, and N. The authors show that arrangement L has the required monoclinic symmetry and M is the structure of the triclinic polymorph. The fair agreement between observed and calculated intensities for these two arrangements based on idealized atomic coordinates, suggests that the proposed monoclinic and triclinic structures are correct. Nevertheless, investigations of micaceous minerals have shown that deviations from the idealized arrangement occur in these structures and that there is also extensive isomorphous substitution taking place in the tetrahedral and octahedral layers of these minerals. This investigation is aimed at the determination of both the distortions and the locations of the isomorphous replacements which exist in the structures.

Structure determination of the monoclinic polymorph

The single-crystal diffraction data for the structure determination of the monoclinic form was collected from a chlorite specimen which had been obtained from the U.S. National Museum and was labeled 'Prochlorite No. 45875'. The sample location is given as 'waterworks tunnel, Washington D.C.'. The chemical analysis obtained in this laboratory for this material is shown in Table 1 and the chemical formula, based on this analysis and assuming 10 oxygen atoms per formula unit, is

$$(Mg_{2\cdot6}Fe''_{0\cdot2}Fe'''_{1\cdot5}Al_{1\cdot2})(Si_{2\cdot2}Al_{1\cdot8})O_{10}(OH)_8\ .$$

Table 1. *Analysis*

Constituent	%	%*
SiO_2	21·7	25·40
MgO	17·0	19·09
Fe_2O_3	20·0	2·86
FeO	2·7	17·77
Al_2O_3	24·4	22·80
CaO	0·4	—
H_2O	—	12·21

* Analysis by Clarke & Schneider (1891).

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* Publication No. 131.

It is noteworthy that the Fe″/Fe‴ ratio in these two determinations is almost completely reversed. This is probably due to the oxidation of the iron after the sample was removed from its location.

The optic sign* of this sample of prochlorite is (+); $2V = 32° 48'$ measured on the universal stage by the direct method; both n_X and n_Y lie between 1·6080 and 1·6209 with the probable value of $n_X = 1{\cdot}610$ and the probable value of $n_Y = 1{\cdot}615$.

X-ray diffraction data from a single crystal with dimensions of approximately 0·1 by 0·15 by 0·05 mm. were collected with both Weissenberg and precession cameras using Cu $K\alpha$ and Mo $K\alpha$ radiations respectively. No corrections for absorption were made on the data. The diffraction symbol was $2/mC$, and space group $C2$ was chosen as being probably correct. The subsequent refinement of the structure showed that this space group is correct. The unit-cell dimensions are

$$a = 5{\cdot}37 \pm 0{\cdot}01,\ b = 9{\cdot}30 \pm 0{\cdot}02,\ c = 14{\cdot}25 \pm 0{\cdot}02\ \text{Å},\ \beta = 96°\ 17' \pm 10'\ .$$

There are two 'molecules' of the above composition in the unit cell; the calculated density is 2·80 g.cm.$^{-3}$ as compared with the observed density 2·85 g.cm.$^{-3}$.

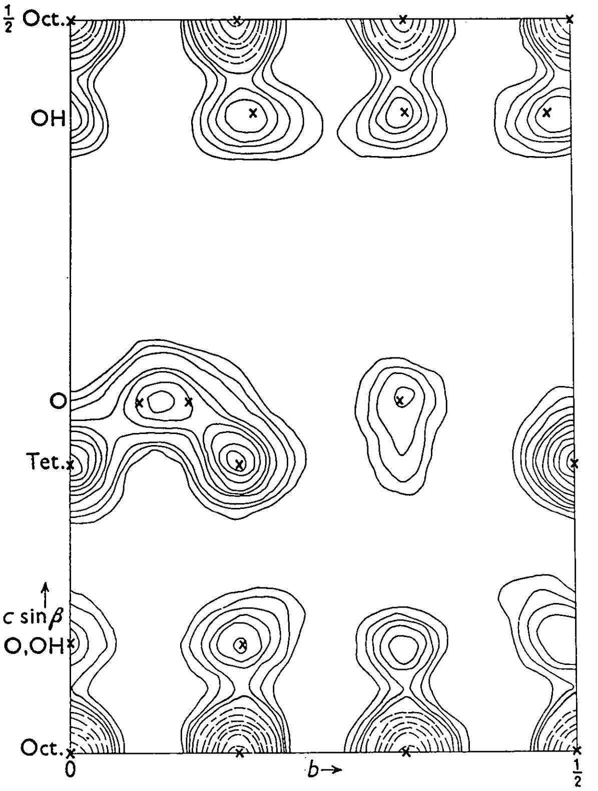

Fig. 1. The (0*kl*) electron-density projection of prochlorite. Contours in intervals of approximately 2 e.Å^{-2}, beginning at 4 e.Å^{-2}. The broken contours are in intervals of 5 e.Å^{-2}. Crosses mark the final locations of the atoms.

The most promising projection for analysis would be down the short a_0 axis of the unit cell. The ideal coordinates, as published by Brindley *et al.*, were assumed and the assumption was also made that the octahedral scattering matter was equally distributed between the talc and brucite layers. The origin of the L structure model was placed off the mirror plane so that the coordinates were acentric. It was hoped that the coordinates which are subsequently recovered from the Fourier projection would show deviations from the ideal parameters and thus fix the space group uniquely. The (0*kl*) Fourier which was recovered from this set of phases showed that all the atoms were, as expected, in essentially correct positions. A notable feature was the rather low peak at $y = \frac{1}{3}$, $z = \frac{1}{2}$ (Fig. 1), which showed that the assumption of equal scattering matter in all the octahedral positions was not correct. A serious drawback of this projection is the lack of resolution of two oxygen atoms which are part of the base of the SiO_4 tetrahedron. Since a distortion of this tetrahedron was suspected—and this Fourier indicated that a distortion was present,

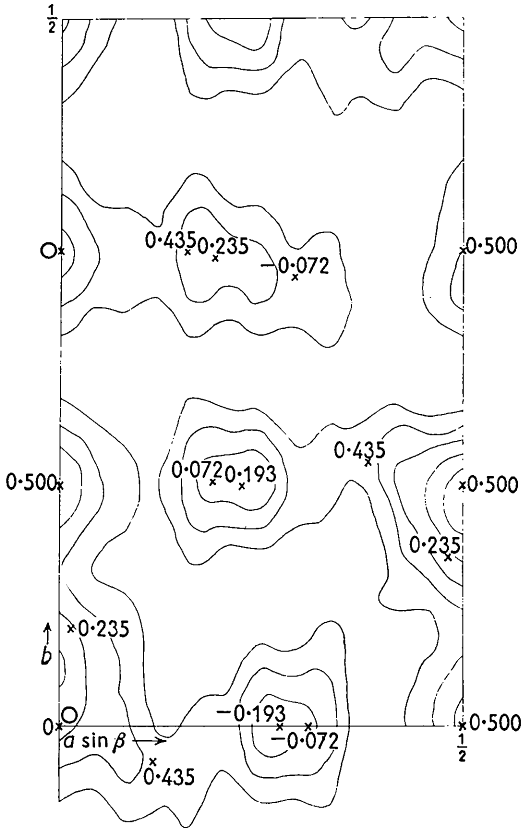

Fig. 2. The (*hk*0) electron-density projection of prochlorite. Contours in approximately 10 e.Å^{-2} intervals, beginning at 10 e.Å^{-2}. Crosses mark the final locations of the atoms, and the numbers give the value of the z parameter of the atom.

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* The optical properties were obtained through the cooperation of M. Friedman of E. and P. Research Laboratory.

because the center of gravity of the superposed oxygens had shifted 0·14 Å from the ideal value—it was decided to investigate this structure by projecting down the long *c* axis. Even though there is a great amount of superposition these critical basal oxygens should appear reasonably well resolved. The final (0*kl*) projection is shown in Fig. 1.

The first set of phases for the (*hk*0) structure factors was again computed on the assumption that all octahedral positions contained equal scattering matter. With this assumption (*hk*0) reflections for which *h* and *k* are both odd do not contain any intensity contributions from the octahedral ion population and it was noted that even though the discrepancy coefficient for all (*hk*0) reflections was about 0·28, the value of *R* for the reflections of *h* and *k* both odd was approximately 0·45. The (*hk*0) projection quite definitely showed unequal peaks for the octahedral ions, and the distortions of the parameters of the basal oxygens were quite evident. Also the hydroxyls of the brucite layer moved a considerable distance from the ideal positions. This projection (Fig. 2) was refined by means of difference syntheses until the discrepancy coefficient for the observed structure factors had decreased to 0·124. As can be seen from the final coordinates listed in Table 2, the positions where isomorphous replacement had occurred could be clearly located.

Table 2. *Final atomic coordinates of prochlorite*

	Atom	*x*	*y*	*z*
A_1*	Mg	0	0	0
A_2	0·75 Mg+0·25 Fe	0	0·333	0
A_3	0·9 Fe	0	0·667	0
A_4	0·75 Al+0·25 Fe	0	0·500	0·500
A_5	0·75 Al+0·25 Fe	0	0·167	0·500
A_6	0·75 Mg	0	0·833	0·500
T_1	0·30 Si+0·70 Al	0·226	0·500	0·193
T_2	0·80 Si+0·20 Al	0·226	0·167	0·193
	O_1	0·190	0·170	0·072
	O_2	0·190	0·500	0·072
	O_3	0·017	0·068	0·235
	O_4	0·517	0·117	0·235
	O_5	0·192	0·328	0·235
	OH_1	0·707	0·314	0·072
	OH_2	0·117	−0·025	0·435
	OH_3	0·157	0·333	0·435
	OH_4	0·117	0·683	0·435

* *A* = octahedral ion, *T* = tetrahedral ion.

The discrepancy coefficient for the (0*kl*) zone is 0·868 (*R*(0*kl*) for the critical reflections $k \neq 3n$ is 0·114). When the coordinates obtained from these two zones are used to compute *R*(*h*0*l*) the value 0·148 is obtained. Calculated and observed values of $|F|$ are listed in Table 3. The atomic scattering factors as given by James & Brindley were used, except for oxygen, where the values given by McWeeny were employed. Weighted scattering factors were used for the octahedral and tetrahedral positions. The temperature factor *B* was evaluated graphically and was 1·7 Å^2 from the (*hk*0) data and 1·5 Å^2 from the (0*kl*) data.

Table 3. *F values*

h k 0	$\lvert F_c \rvert$	F_o
0 2 0	77	78
4	15	18
6	209	212
8	15	48
10	21	23
1 1 0	18	15
3	51	58
5	17	*
7	27	25
9	9	*
11	19	18
2 0 0	28	44
2	44	48
4	32	44
6	10	18
3 1 0	33	32
3	36	39
5	41	46
7	7	*
9	9	*
4 0 0	112	110
2	40	39
4	6	*
6	61	67
8	18	18
5 1 0	28	37
3	31	35
5	12	*
7	29	28
6 0 0	43	58
2	6	*
4	14	18

0 *k l*	$\lvert F_c \rvert$	F_o
0 0 1	61	52
2	124	132
3	96	101
4	205	198
5	106	109
7	63	64
9	46	49
10	81	87
12	84	76
14	75	60
16	87	60
0 2 0	77	78
1	31	16
2	52	54
3	47	35
4	42	37
5	34	33
7	40	39
0 4 2	47	39
3	26	29
4	32	39
6	47	45
8	49	47
10	35	35
11	30	33
13	35	37
0 6 0	209	212
1	31	23
2	95	101
3	39	43
4	80	76
5	45	49
6	58	60
7	22	25
10	75	70
11	36	35
12	48	47
14	54	52
16	61	52
0 8 6	33	31
10	27	29
0 12 0	65	68
2	23	29
4	32	37
6	27	27

* Reflection not observed.

Discussion

The detailed investigation of these minerals was undertaken with the following aims in mind: (1) To what extent do the atomic coordinates for the monoclinic and triclinic chlorites differ from the 'ideal' structures? (2) What is the distribution of ions which replace part of the magnesium and silicon within the talc and brucite layers? Is the substitution random or is there preferential concentration of these ions in certain sites? Will it be possible to detect aluminum ions in the tetrahedral sites, where they might occupy definite positions in the structure, or are they statistically distributed over the tetrahedral holes?

The results that have become available from this investigation seem to supply definite answers to these problems. Figs. 1 and 2 show that the peak heights of the ions in octahedral coordination are not uniform. When this information was subsequently used in the computation of structure factors the agreement between F_o and F_c rapidly improved over what it had been when the phases were computed on the basis of uniform scattering in all octahedral sites. Not only was it possible to differentiate between the scattering material in the brucite and the talc layers, but within the octahedral positions of each unit the $(F_o - F_c)$ syntheses showed a decided ordering of ions in definite sites, as shown in Table 2. Of particular interest is the distribution of bond distances in the tetrahedral layer. One set of distances has an average value of $1{\cdot}72_6$ Å and the other three distances show an average of 1·64 Å (Table 4). This strongly implies that there is a preferential concentration of aluminum ions in alternate sites in the tetrahedral layer, and if one makes use of the curve published by Smith (1954) then there is approximately 70% aluminum in tetrahedral position 1 and about 22% Al in the other site. It is not possible to resolve the interesting question of whether this represents a stage wherein the aluminum is tending toward a random tetrahedral distribution or whether it is a stage in the reverse process whereby the aluminum from an originally random distribution is segregating into definite locations in the structure. The similar problem of the position of tetrahedral aluminum presents itself in the structure of muscovite mica, where one out of three sites is occupied by aluminum. Unfortunately no precise determination of this structure has ever been published.

Table 4. *Bond lengths and angles*

	T_1–O_5	1·73 Å		T_2–O_5	1·63 Å
	T_1–O_4	1·72		T_2–O_4	1·68
	T_1–O_3	1·73		T_2–O_3	1·62
Average	T_1–O	$1{\cdot}72_6$	Average	T_2–O	1·64
	T_1–O_2	1·71		T_2–O_1	1·71

A_1–O_1	2·08 Å	A_2–O_1	2·05 Å	A_5–OH_2	2·14 Å
A_1–O_2	2·05	A_2–O_2	2·07	A_5–OH_3	2·04
A_1–OH_1	2·24	A_2–OH_1	1·98	A_5–OH_4	2·17
A_2–O_1	2·04	A_4–OH_2	2·17	A_6–OH_2	1·77
A_2–O_2	2·07	A_4–OH_3	2·04	A_6–OH_3	1·97
A_2–OH_1	1·98	A_4–OH_4	2·07	A_6–OH_4	1·82

Average	O–H–O	2·92 Å
Average	∠ O–T–O	110·8°
Average	∠ T–O–T	133·8°

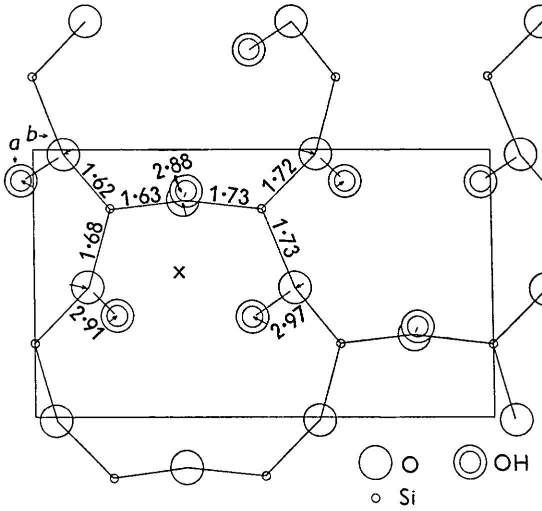

Fig. 3. The Si–O net and the brucite OH positions in prochlorite projected on the basal plane. The arrows indicate the amount of shift of the atoms away from the 'ideal' position to the location determined in this study.

Some of the atomic parameters of Table 2 deviate considerably from the 'ideal' values previously used for this structure. The deviations for the oxygen parameters forming the base of the tetrahedral layer are produced by a rotation of the (Si, Al)–O tetrahedron, as shown in Fig. 3. Another marked deviation exists for the parameters of the hydroxyls of the brucite layer. As a result, the hydrogen bond between the tetrahedral basal oxygen and the hydroxyl of the brucite layer becomes much stronger and the distance between the two layers decreases to an average value of 2·92 Å as compared to a distance of 3·07 Å when the 'ideal' coordinates are used. The shift of the hydroxyl groups also gives rise to another interesting observation. From the peak heights it had been determined that octahedral position 6 in the brucite layer, marked by a cross in Fig. 3, was occupied on the average only three-fourths of the time. The bond distances computed for the magnesium located in this site and its octahedrally coordinated hydroxyl groups are considerably shorter than the distances observed for the bonds between OH groups and the ions in the other two sites. Thus the two triads of OH groups tend to draw closer together around the partially occupied octahedral site and at the same time by this shift approach the basal oxygen atoms above and below them to form a tighter hydrogen bond than would otherwise be possible (Fig. 3). The bond length between the tetrahedral ion and the apical oxygen which participates also in octahedral coordination is 1·71 Å. The O–(T)–O angles are tetrahedral and the (T)–O–(T) angle is 133·8°.

From the structural analysis of this chlorite specimen the cation distribution in the octahedral and tetrahedral sites becomes

$$(Mg_{2\cdot5}Fe_{1\cdot65}Al_{1\cdot5})(Si_{2\cdot2}Al_{1\cdot8})O_{10}(OH)_8\,,$$

which is in good agreement with the formula derived from the chemical analysis. If the assumption is made that most of the iron was originally present in the ferrous state—and the analysis by Clarke & Schneider (Table 1) supports this assumption—then the negative charge on the talc layer arises from the isomorphous replacement of the silicon in the tetrahedral sites. All the octahedral sites of the talc layer are thus available to divalent ions, but the number of divalent ions in the brucite layer is limited, with the rest of the octahedral positions filled with trivalent ions. The excess positive charge which is thus imparted to the brucite layer neutralizes the charge on the talc layer in the same manner as the potassium ion in the mica structure. In the oxidized chlorite specimen, however, the charge distribution will be altered because most of the ferrous iron will become trivalent and part of the excess negative charge in the talc layer is now compensated by the increased positive charge on the octahedral talc layer. A possible mechanism for keeping the structure neutral would be for some of the hydroxyl groups of the brucite layer to lose hydrogen ions. Thus weathering of a high-iron chlorite could lead to a preferential attack on the brucite layer and subsequently produce other types of clay minerals.

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The Crystal Structure of Chlorite. II. A Triclinic Polymorph*

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The crystal structure of the triclinic chlorite corundophillite differs from the monoclinic polymorph prochlorite in the stacking of the two Si–O layers in the talc portion of the structure. Shifting of the SiO_4 tetrahedra away from their ideal positions occurs also in this structure. The isomorphous substitution occurs at random in this structure. The brucite layer is held to the talc layer by hydrogen bonds, which are 2·92 Å long. The neutralization of the charge arising in the tetrahedral layer is compensated by isomorphous substitution in the octahedral positions of both the talc and brucite layers.

Introduction

The analysis of the structure of a chlorite in Part I (Steinfink, 1958) has confirmed the *L* structure postulated for it by Brindley, Oughton & Robinson (1950), but in addition has demonstrated that a rotation of the Si–O tetrahedra, together with other deviations from the ideal coordinates, exist. It has also shown a rather high degree of ordering of cations which replace the magnesium and silicon ions in the octahedral and tetrahedral sites respectively. The structural investigation of a triclinic polymorph with a composition very close to that of an 'ideal' chlorite should thus provide information about the influence of isomorphous substitution on ordering and on the extent of deviation of atomic parameters from their ideal values.

Experimental determination of the structure

The single-crystal diffraction data for the structure determination of the triclinic polymorph were collected from a chlorite specimen obtained from the Harvard University collection. It was labeled 'Corundophillite from the Mochako District, Kenya'. The chemical analysis obtained in this laboratory is shown in Table 1 and the chemical formula, based on this analysis and assuming 10 oxygen atoms per formula unit, is

$$(Mg_{4\cdot9}Al_{0\cdot75}Fe'''_{0\cdot17}Fe''_{0\cdot07}Cr'''_{0\cdot18})(Si_{2\cdot6}Al_{1\cdot4})O_{10}(OH_8)\ .$$

Table 1. *Analysis*

Constituent	%
SiO_2	27·4
Fe_2O_3	2·4
FeO	0·8
Al_2O_3	18·9
Cr_2O_3	2·3
MgO	34·0

The optic sign of this sample of chlorite is (+): $2V = 44° 45'$, and was measured on the universal stage by the direct method; both n_X and n_Y lie

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* Publication No. 134.