

RELATIONSHIPS BETWEEN THE MINERAL ASSOCIATION, CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF THE CHLORITE SERIES¹

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ABSTRACT

Relations between the geologic association, chemical composition, and optical properties of over 200 analyzed chlorites are shown graphically. The range of composition for an individual geologic association is quite restricted as compared to the entire compositional range possible for chlorite. Nearly all of the Al values fall between 2 and 3 atoms per ten cations, but the Al value for chlorite from mafic igneous rocks and from high-Cr associations is distinctly low. In groups in which chlorite is essentially a rock-forming mineral the composition is about what one would expect from the composition and mineralogy of the rock; high Mg in ultramafic associations, high Fe in iron-formations, high Fe³⁺ accompanying high Fe, etc. The compositional range is larger in the other groups, especially that for Fe³⁺, but the Fe³⁺: Fe ratio is nearly constant.

Of the 73 samples in those groups in which chlorite is essentially a rock-forming mineral, 82 per cent have a $(\text{Fe} + \text{Mn} + \text{Cr}) / (\text{Fe} + \text{Mn} + \text{Cr} + \text{Mg})$ ratio which deviates less than 0.05 from a fitted curve for β . This curve also fits the data for the other groups fairly well although there is considerably more general deviation; but chlorite from amygdules and veins in mafic igneous rocks deviate seriously. Chlorite of most associations changes sign at a β index of about 1.630 and a Fe/(Fe+Mg) value of 0.52. Chlorite with β greater than about 1.630 has a higher iron content, a negative optic sign, is length slow, and displays abnormal violet or blue interference colors near the sign change. Chlorite with β less than about 1.630 has a lower iron content, a positive optic sign, is length fast, and displays abnormal brown interference colors near the sign change. Birefringence increases with both increasing and decreasing refractive index away from the sign change. In routine petrographic work the optic sign and interference colors may be used to estimate Fe/(Fe+Mg) for most associations. However, chlorite from amygdules and veins in mafic igneous rocks deviate from these generalizations. The Al-content of chlorite cannot be estimated from the optical properties, but can be approximated from d(001).

INTRODUCTION

The mineral chlorite has a structure which permits extensive isomorphic substitution, hence it has a wide range of chemical composition. Varieties have been quite arbitrarily defined within the chlorite series (Winchell, 1936; Orcel, 1927, 1959; Hey, 1954; Nelson and Roy, 1954; Phillips, 1954; and Lapham, 1958), much as has been done with the plagioclase series.

A number of attempts have been made to relate the chemical composition and optical properties of chlorite (Winchell, 1936; Orcel, 1927; Hödl, 1941; Serdyuchenko, 1953, and Hey, 1954), and an optical classification of the chlorite series was presented by Winchell (1936). Complications of analyses or sources of analyses have been published by Orcel (1927),

¹ Publication authorized by the Director, U. S. Geological Survey.

Winchell, (1936), Serdyuchenko (1953), and Hey (1954). The relationship between the *x*-ray properties and the chemical composition has been investigated by Engelhardt (1942), Bannister and Whittard (1945), Hey (1954), Mikheev (1953), Brown (1955), Brindley and Gillery (1956), Phillips (1954), Kovalev (1956), Lapham (1958), and Shirozu (1958a, 1960). Structural analyses have been reported by Pauling (1930), McMurchy (1934), Garrido (1949), Brindley, Oughton and Robinson (1950), Brindley and Robinson (in Brindley, 1951) and Steinfink (1958). Tuddenham and Lyon (1959) investigated the relation between infrared spectra and chemical composition of chlorite. Hydrothermal investigations on the stability of Mg-chlorite have been reported by Yoder (1952) and by Nelson and Roy (1954, 1958). Turnock (1960) investigated the stability of Fe-chlorite.

A knowledge of the chemical composition of chlorite, especially the Fe/(Fe+Mg) ratio, is particularly important in the study of phase relationships in low- and middle-grade metamorphic rocks, in as much as knowledge of the relative values of this ratio in coexisting mineral pairs limits the possible configurations on phase diagrams. Such information must be obtained for a great number of coexisting pairs in different occurrences and the cost of obtaining these data by chemical analysis may be prohibitive. Because only relative values of Fe/(Fe+Mg) are necessary, this ratio may be determined with sufficient accuracy by optical measurements.

The present study was begun with the hypotheses that the refractive index of chlorite depends primarily upon the Fe content, and that the variation of other components which affect the index (Al, Fe³⁺, Ti, Mn, Cr, etc.) is restricted by the mineral assemblage. Data are not available to study chlorite of specific mineral assemblages, but it was believed that groups of differing mineralogic or geologic association could be chosen which would somewhat restrict the variation. If so, a diagram relating Fe/(Fe+Mg) and the optical properties for chlorites from a given association or group of associations should be more accurate than one prepared for chlorites in general. Moreover, it is extremely useful to know what chemical composition of chlorite is expectable in a given association.

SOURCE AND GROUPING OF DATA

Over 200 analyses of chlorite taken from the literature and about a dozen derived from various unpublished sources were used in this study. Only one of the analyses used was made before 1900; other analyses were rejected if the geologic occurrence or optical properties were not given, unless *x*-ray data were given. Analyses calculated from

the chemical composition and mode of the host rock have not been included.

It would be desirable to discuss the properties of chlorite by specific mineral assemblages as this would place the greatest restriction on the range of composition. Data are not available to do this, but it was possible to place 130 of these analyses into 13 groups of different geologic occurrence or mineral association which have significantly restricted ranges of composition.

Groups Ia–If include most of the associations in which chlorite would be classed as a “rock-forming mineral,” and, as will be shown, includes those associations which show a very good correlation between optical properties and $Fe+Mn+Cr/Fe+Mn+Cr+Mg$.¹ The 15 groups used and the distribution of samples in the groups are summarized in the following section:

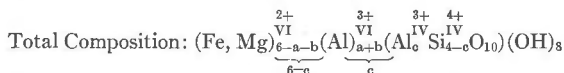
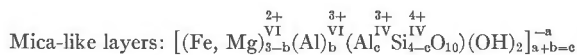
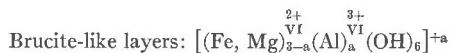
- Group Ia includes 17 chlorites associated with quartz and white-mica, mainly from schist, and 2 chlorites from quartz-biotite schist.
- Group Ib includes 14 chlorites from greenstone and amphibolite.
- Group Ic includes 7 chlorites associated with the magnetite, hematite, Fe-carbonate, etc., of iron-formation.
- Group Id includes 21 chlorites associated with talc, serpentine, or from the “blackwall” chlorite zones at the borders of metamorphosed serpentinite masses.
- Group Ie includes 7 chlorites from quartz-free, corundum, margarite, spinel, diaspore, etc., assemblages and one chlorite from bauxite.
- Group If includes 10 chlorites associated with carbonate rocks; 4 are from talc-magnesite rock and the others are from metamorphosed dolomite or limestone and are associated with various magnesium-calc-silicates.
- Group IIa includes 7 chlorites from the border zones of albite pegmatites enclosed in serpentinite masses.
- Group IIb includes 10 chlorites associated with quartz in veins of various occurrences.
- Group IIc includes 8 chlorites associated with metallic ore deposits and separated from Group IIb because quartz is not cited in the association.
- Group IIId includes 4 chlorites from veins in granite and one from chlorite-muscovite clots in an albite dike in paragneiss.
- Group IIE includes 11 chlorites from mafic igneous rocks; 7 are from amygdule fillings in mafic volcanic rocks and the others are from fractures in diabase, diorite, or trap rock.
- Group IIIa includes 33 chlorites from unknown associations or from associations for which there were not enough samples to make up a group. Most of these are included because *x*-ray data are available for them. The group also serves as a check as to whether the above groups include the entire compositional range of chlorite.
- Group IIIb includes 4 chlorites associated with Mn-minerals.
- Group IIIc includes 8 chromium chlorites ($Cr_2O_3 > 2$ weight per cent).
- Group IIId includes 32 samples selected from Serdyuchenko (1953). These are from the samples which he described individually and for most of which he gives

¹ $Fe+Mn+Cr/Fe+Mn+Cr+Mg$ in per cent is abbreviated by F/FM throughout the remainder of the paper.

optical, x-ray, and DTA data. A few such were not included because the analysis could not be reduced to any semblance of a chlorite formula. This group is not considered further in this paper because the analyses as a group show gross discrepancies from the ideal formula of chlorite and from the correlations based on analyses from all other sources.

STRUCTURAL CHEMISTRY OF CHLORITE

The chlorite structure consists of an alternating series of brucite-like layers and mica-like layers. In the ideal scheme, which was originally suggested by Pauling (1930, p. 578), the mica-like layer is negatively charged due to the replacement of Si by Al in four-fold position. This negative charge is balanced by a corresponding number of Al atoms replacing divalent ions in the six-fold position in the brucite-like layer. This ideal structural formula, with coordination numbers given by Roman superscripts and charges in Arabic superscripts, is:



In general, as indicated in the total composition formula, the distribution of six-fold Al between the mica-like and the brucite-like layers cannot be determined.

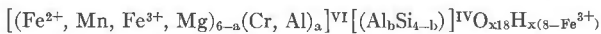
Most analyses of natural chlorites report some Fe^{3+} as well as small amounts of Mn, Ti, Cr, Ca, Na, and K. Mn and possibly small amounts of Ca substitute directly for Fe and Mg in the six-fold position. Because of the difference in ionic radii it is believed that most of the Ca reported in analyses of chlorite is due to impurities in the sample, although it has been suggested that in some chlorites it may be held between the layers (Gruner, 1944, p. 428-429). Na and K are also very likely present in impurities but small amounts may be held between the layers. However, K-Ar age determinations are commonly undisturbed by partial alteration of biotite to chlorite, indicating that little or no K is retained by the chlorite. Much of the Ti is in fine inclusions of rutile, ilmenite, and sphene that are commonly present in chlorite, but small amounts may substitute in the six-fold position. Fe^{3+} and Cr, as well as Ti, may substitute in the six-fold position, with the charge difference balanced by Al (or very small amounts of Fe^{3+} and Ti) entering four-fold coordination in the place of Si or by vacancies in the six-fold position.

A. N. Winchell (1926, 1936), Dschang (1931), Brindley and Youell (1953), and others have shown that the state of oxidation of the iron in chlorite may be changed without destruction of the crystal structure and that the process is reversible. Much, perhaps most, of the Fe^{3+} reported in analyses of chlorite seems to have been originally Fe^{2+} which has been oxidized with loss of H from hydroxyl groups.

Several other substitution mechanisms and structural complications are conceivable, including: additional H or interlayer Ca balanced by vacancies in the six-fold coordination position; differing distribution of six-fold cations between the brucite-like and mica-like layers; the presence of dioctohedral gibbsite-like or mica-like layers; the presence of four-fold hydroxyl; and the replacement of OH by F and Cl.

The analyses used in this study were recalculated into cation-numbers per 10 cations, exclusive of H, Cl, and F, and of Ca, Na, K, and Ti. As indicated above, the reported K, Na, and Ca are believed to be present in mineral impurities rather than in the chlorite. Ti was also excluded from the summation to 10 cations, although it may be present in the chlorite structure in some instances. From personal experience the author knows that it is almost impossible to remove the fine-grained rutile, sphene, and ilmenite commonly present in chlorite. About two-thirds of the analyses reported TiO_2 , ranging from 0.00 to 1.00 weight per cent. The average is 0.169 weight per cent, but 22 analyses reported TiO_2 absent or present only in trace amounts. Three analyses with higher TiO_2 contents were excluded because the original author indicated that the TiO_2 was present in impurities. At any rate, the average and the maximum values correspond only to about 0.02 and 0.1 atoms per 10 cations, respectively, and would not seriously affect the results.

Chlorite analyses recalculated in terms of cation numbers per 10 cations correspond to a structural formula based on the assumption that all 6 six-fold and all 4 four-fold coordination positions are filled. Such a formula has the following form:



Part of the Al is assigned with the Si to fill the 4 four-fold positions and the remainder assigned to the six-fold positions. The following discussions will be in terms of cation numbers in this formula, but the values can also be interpreted as cation numbers per 10 cations or as cation percentages (exclusive of H), if multiplied by ten.

It should be noted that the various charts relating composition and optical properties in chlorite (*i.e.* Winchell, 1936; Hey, 1954) imply that simultaneously, $\text{Si} + \frac{1}{2}\text{Al} = 4$, that no vacant positions exist, and that all the Fe^{3+} is balanced by loss of H. How well these conditions are satisfied

is indicated by Fig. 1 on which the charge imbalance due to unequal partition of Fe^{3+} , Al, and Cr between the six-fold and the four-fold coordination positions, $(x-y) = (\text{Fe}^{3+} + \text{Al} + \text{Cr})^{\text{VI}} - \text{Al}^{\text{IV}}$, plotted against H content (z). The symbols x , y , and z refer to the formula on Fig. 1 and are in cation numbers per 10 cations. The 115 analyses on Fig. 1 include those for which there is no real reason to suspect the quality of the analysis or the purity of the mineral separate. Analyses with $\text{K}_2\text{O} + \text{Na}_2\text{O} > 0.50$ per cent, $\text{CaO} > 1.00$ weight per cent, or $\text{Cr}_2\text{O}_3 > 2.00$ weight per cent were excluded from this group. Fifty-one of the analyses used are believed, on the basis of the published description or personal knowledge of the sample purity and analytical quality, to be of high quality. They are indicated by the larger dots and are more heavily weighted in the following considerations.

Structural formulas whose $(x-y)$ and (z) values fall on the line $(x-y) = (8-z)$ in Fig. 1 have a total cation charge of 36, no charge imbalance $(x-y)$ except that compensated by gain or loss of H, and a full complement of OH, except that gained or lost to compensate for the charge imbalance $(x-y)$. Positive values of $(x-y)$ on this line are produced by the mechanism of Fe^{2+} going to Fe^{3+} , balanced by loss of H,

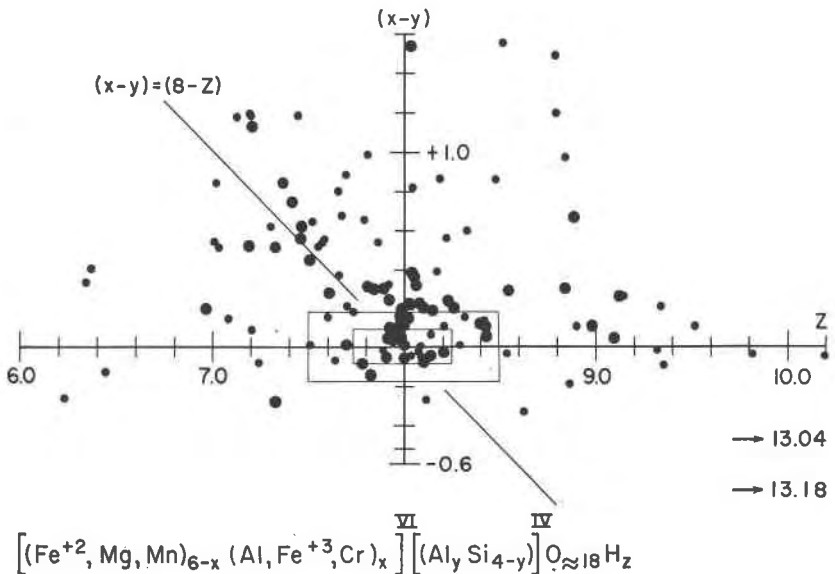


FIG. 1. Relationship between the charge imbalance $(x-y)$ due to unequal partition of Fe^{3+} , Al and Cr between the six-fold and four-fold coordination positions and H content of chlorites. x , y , and z refer to the formula given and are in cation-numbers per 10 cations. More reliable analyses are shown by the larger dot (see text).

and negative values by the mechanism of adding H to balance excess negative charge in the structure. The analyses plotted on Fig. 1 exhibit notable departures from this ideal formula of chlorite.

In common practice structural formulae of chlorite are calculated by, in effect, setting the sum of the cation charges, excluding H, to 28 ($O=10$, $OH+F+Cl=8$). Points with positive $(x-y)$ values in Fig. 1 would have vacant positions and lower $(x-y)$ values if calculated by this procedure; points with negative $(x-y)$ values would contain more cations than the available positions if calculated by this procedure.

The deviations from the ideal values are not explainable by "normal" errors in chemical analysis. As analytical error appears to vary with concentration, a relative deviation for each oxide at the concentration level found in chlorite was approximated following a method suggested in part by Ahrens (1954). The standard deviation and twice the standard deviation for "normal" analytical errors in $(x-y)$ and z were calculated for a typical chlorite analysis and are shown as rectangles on Fig. 1.

Many of the erratic points could be explained by gross error in the H value or in the Fe^{2+} value. Such gross errors in the H values are expectable, owing to the difficulty of distinguishing hydroxyl water from inter-layered or adsorbed water and to the difficulty of making an accurate correction for oxidation of FeO during analysis of hydrous iron-silicates. Indeed, many of the analyses report only total water and very few report F or Cl. The error in Fe^{2+} in G-1 and W-1 (Fairbairn, 1953, p. 146) is large and gross errors are possible in this determination. Other grossly erratic points may be related to the difficulty of preparing pure chlorite concentrates from many of the more common assemblages in which chlorite is found. An admixture of quartz or muscovite in the chlorite sample, for example, would produce a positive value of $(x-y)$ whereas an admixture of talc or serpentine would produce a negative value. Many of the higher Al values do have large positive values and many of the lower Al values have large negative values of $(Al+Cr)^{VI}-Al^{IV}$.

The median for points in Fig. 1, not considering the grossly erratic points, is clearly above the line for the ideal values, which might suggest that some vacancies are commonly present. However, the median for $(Al+Cr)^{VI}-Al^{IV}$ is close to zero, not considering the grossly erratic points, suggesting that the positive value of the median on Fig. 1 is a result of too high values of OH rather than of vacancies in the six-fold position and that essentially all the Fe^{2+} is balanced by loss of H.

It might be expected that the refractive indices or specific gravity would be lowered by the presence of an appreciable number of vacancies. A good correlation exists between F/FM and β , but the deviations do not correlate with $(Al+Cr)^{VI}-Al^{IV}$. Similarly the relationship between

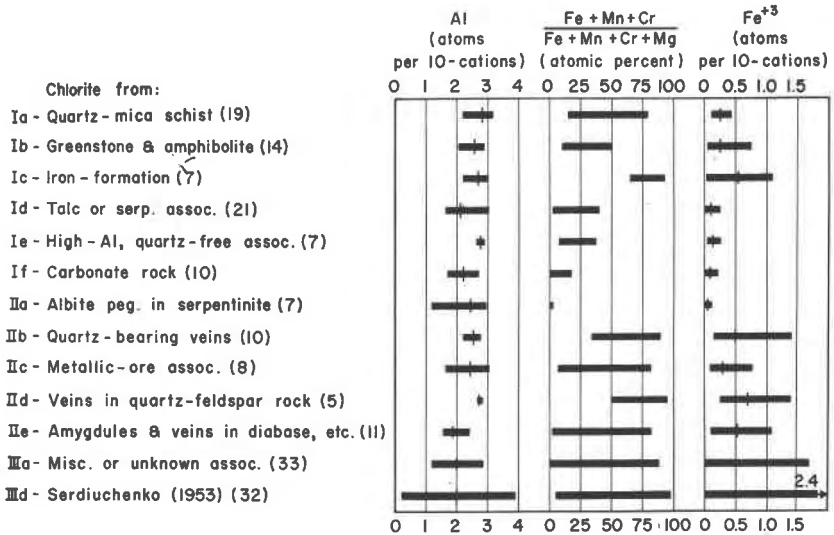


FIG. 2. Some relationships between geologic or mineralogic association and chemical composition of chlorite. The range of values is indicated by the bar and the arithmetic average by the cross-bar.

specific gravity, F/FM , and $(Al+Cr)^{VI}-Al^{IV}$ was plotted for 66 samples. Although there is a clear correlation between density and F/FM , there are many large deviations. The deviations do not correlate with $(Al+Cr)^{VI}-Al^{IV}$ as might be expected if $(Al+Cr)^{VI}-Al^{IV}$ truly represented cation vacancies, but the experimental error is clearly too large to make this a positive test for the presence of vacancies.

RELATIONS BETWEEN THE CHEMICAL COMPOSITION AND MINERAL ASSOCIATION OF CHLORITE

Some relationships between chemical composition and geologic or mineralogic association of chlorite are summarized on Fig. 2 and in Table 1. The range of values is indicated on Fig. 2 by the bar and the arithmetic average by the cross-bar. Relationships between these parameters were examined by triangular plots for each group, but provided only limited information which is included below.

Nearly all the Al values fall between 2 and 3 atoms per 10 cations, although the Al value might well range from 0 to 4, as it does in the septechlorite series from antigorite to amesite. The differences in sizes of silicon- and aluminum-occupied tetrahedra, and of iron-, magnesium- and aluminum-occupied octahedra indicates that there must be an optimum range of aluminum substitution for the best fit of these two

TABLE 1. SOME RELATIONSHIPS BETWEEN GEOLOGIC OR MINERALOGIC ASSOCIATION AND CHEMICAL COMPOSITION OF CHLORITE

Group	Atoms per 10 Cations												Percent										
	Al			Mg			Fe ²⁺			Fe ³⁺			1		2		3						
	Mn	Av	Mx	Mn	Mx	Mn	Mx	Av	Mn	Mx	Av	Mn	Mx	Mn	Mx	Av	Mn	Mx	Av	Mn	Mx		
Ia (19)	2.2	2.84	3.1	1.1	4.0	0.5	3.3	0.1	0.25	0.4	.002	.042	.15	(17)	15	79	5	12.5	22	0.1	2.41	11.6	
Ib (14)	2.1	2.57	2.9	2.3	4.4	0.4	2.3	0.1	0.27	0.8	.002	.023	.04	(11)	11	51	1	15.0	33	0.4	1.18	2.5	
Ic (7)	2.2	2.71	3.0	0.4	1.6	2.4	4.1	0.1	0.55	1.1	.00	.003	.005	(8)	65	92	1	14.4	31	0.0	0.09	0.2	
Id (21)	1.7	2.12	3.0	2.9	4.8	0.1	1.8	0.0	0.10	0.3	.00	.016	.08	(19)	3	40	0.2	16.4	47	0.0	3.67	27.7	
Ie (7)	2.6	2.77	2.9	2.9	4.4	0.2	3.7	0.0	0.13	0.3	.002	.020	.08	(6)	8	37	4	15.4	34	0.1	1.32	4.9	
If (10)	1.7	2.21	2.7	3.7	5.2	T	0.7	0.0	0.09	0.2	.00	.013	.04	(3)	0	18	17	45.7	84	0.0	—	16.0	
IIa (7)	1.2	2.45	2.9	4.2	5.4	T	.03	0.0	0.06	0.1	.00	.007	.02	(3)	0.6	3	35	77.7	100	0.0	—	50.0	
IIb (10)	2.2	2.55	2.8	0.5	3.3	1.4	3.6	0.2	0.50	1.4	.00	.062	.27	(9)	34	89	5	17.1	66	0.0	1.72	6.6	
IIc (8)	1.6	2.42	3.0	0.9	4.8	0.2	3.8	0.1	0.30	0.8	.005	.020	.04	(7)	7	81	7	14.5	34	0.0	1.63	7.1	
IID (5)	2.7	2.71	2.8	0.2	2.3	1.4	3.6	0.3	0.69	1.4	.00	.030	.05	(3)	52	95	8	25.1	50	0.2	—	1.4	
IIe (11)	1.6	1.89	2.4	0.8	4.5	0.3	2.9	0.1	0.53	1.1	.005	.040	.12	(9)	2	82	12	30.6	73	0.2	2.08	3.9	
IIIa (33)	1.2	—	2.9	0.6	5.3	0.0	3.3	0.0	—	1.7	.00	.049	.35	(30)	1	87	1	32.8	100	0.1	3.35	31.6	
IIId (32)	0.3	—	3.9	0.1	5.4	0.1	3.7	0.0	—	2.4	.00	—	.04										

$$1) \frac{\text{Fe}+\text{Mn}+\text{Cr}}{\text{Fe}+\text{Mn}+\text{Cr}+\text{Mg}}$$

$$2) \frac{\text{Fe}^{3+}}{\text{Fe}+\text{Mn}+\text{Cr}}$$

$$3) \frac{\text{Mn}}{\text{Fe}+\text{Mn}+\text{Cr}}$$

types of layers (Brindley, 1955; Bradley, 1959). For trioctahedral layered silicates the optimum range of Al^{IV} should be about 1.0–1.8 (Bradley, 1959, p. 23), an Al value in atoms per 10 cations of about 2.0–3.6. For the analyses used in this study 2.6–2.7 is approximately the medial value for Al. Moreover, Al values greater than 2.7 have the largest positive $(\text{Al}+\text{Cr})^{\text{VI}}-(\text{Al})^{\text{IV}}$ values and Al values lower than 2.6 have the largest negative values. This suggests that the higher and lower Al values are due in part to impurities or analytical errors in Al_2O_3 or SiO_2 .

Despite this structural restriction on the range of Al substitution the Al content does correspond to the mineral association. Chlorite, or any mineral with a range in Al content, should have its highest Al content in association with high-Al minerals and its lowest Al content in association with low-Al minerals; this may be seen most simply by a consideration of phase diagrams. Chlorites from talc and serpentinite associations, from carbonate rock associations, and from high-Cr associations have a relatively low Al content; those associated with muscovite, corundum, margarite, spinel, diaspore, etc. have a relatively high Al content. The 1.9 average Al value for chlorite from amygdules and veins in mafic igneous rocks (Group IIe) is distinctly low, and it is not clear why it is so much lower than for chlorite from serpentinite-talc associations. However, many of the latter are from "blackwall" reaction zones at the contacts of ultramafic masses and may have derived their Al from adjacent more-aluminous rock. Similarly the Al value of chlorites from high-Al, quartz-free associations (Group Ie) might be expected to be distinctly higher than for other associations, but this is not the case.

No general correlation seems to exist between the Al value and F/FM. However, chlorites with extremely low F/FM values do have a wide range of Al values, as is exemplified by Group IIa.

Chlorite may have any proportion of Fe to Mg; the exact value depends both upon the Fe:Mg ratio in the bulk rock and upon the nature of the other minerals among which the Fe and Mg are partitioned. The Fe:Mg ratio in the first six groups of chlorites, those in which chlorite is essentially a rock-forming mineral, and in Group IIa is about what one would predict from the composition of the rock; high Mg in ultramafic associations, high Fe in iron formation, etc. The range of Fe:Mg is much larger in other groups, such as veins, in which no limit is placed on Fe:Mg by a restricted range of total-rock composition.

The range of Fe:Mg in Groups Ia and Ib is of particular interest because of the abundance of quartz-mica schist, greenstone, and amphibolite. In both quartz-mica schist and greenstone chlorite may constitute a major portion of the rock with no other Fe-Mg-silicate associated with it. In such rocks the chlorite essentially reflects the bulk Fe:Mg

composition of the rock since the Fe:Mg range in chlorite is restricted only by the range found in the rock. This range will be further restricted by the coexistence of other Fe-Mg phases. Biotite, garnet, staurolite, chloritoid and, of course, Fe-oxides contain higher Fe:Mg ratios than does associated chlorite; actinolite and hornblende commonly contain a slightly lower Fe:Mg ratio. In general, chlorite is more magnesium-rich in higher grades of metamorphism. This generalization is supported by experimental work (Nelson and Roy, 1958; Turnock, 1960) which indicates that the maximum stability temperature of Mg-chlorite is higher than that of Fe-chlorite.

Ferric iron ranges from 1 to 1.7 atoms per 10 cations. Except for chlorite from Fe-formation (Group Ic), the chlorites of Groups I and Group IIa have a restricted, low range of Fe^{3+} values (the 4 high values in Group Ib are from veinlets in amphibolite rather than from the matrix of the rock). High Fe^{3+} values accompany high Fe^{2+} and high F/FM. Figure 3 shows the relationship between Fe^{3+}/F , and F/FM. Fe^{3+}/F is nearly constant for F/FM values greater than 10 per cent; below 10 per cent analytical error accounts for the much wider range. The average Fe^{3+}/F value for the 61 Group I analyses with F/FM > 10 per cent is 0.137 ($\sigma=0.086$); for 50 analyses of Group II and IIIa, 0.227 ($\sigma=0.186$). Fe^{3+} content correlates better with total Fe than with specific geologic or mineralogic association, possibly reflecting oxidation of a relatively constant proportion of the total Fe.

The Mn content differs greatly from group to group, but the maximum value is only 0.3 atoms per 10 cations (2.75 weight per cent). Four analyses are available of chlorite associated with Mn-minerals. One of these samples is truly a Mn-chlorite; it contains 38.93 weight per cent MnO (Mn, 3.97) and its crystals are orange-red. However, a sample with a Mn value of 0.08 (MnO=1.06 weight per cent) also has orange-red crystals and a sample with a Mn value of only 0.05 (MnO=0.69 weight per cent) has light brown crystals with a pink tinge. The color of the other sample was not given.

Many chlorites in the other groups have more MnO than these in this group, but the orange-red color does not appear if the samples are also high in Fe. The orange-red color characteristic of "Mn chlorite" is more a function of Mn/Fe than of Mn content.

Mn shows a better correlation with the geologic or mineralogic association than with F/FM. Fifty-three Group I chlorites with F/FM > 10 per cent have an average Mn/F of 0.016 ($\sigma=0.022$), and 41 Group II chlorites 0.015 ($\sigma=0.017$). The standard deviation is larger than the average, whereas there is a 14-fold difference in the average Mn value for Groups Ia-Ic.

Lapham (1958) indicated that Cr substitution less than 1-2 weight

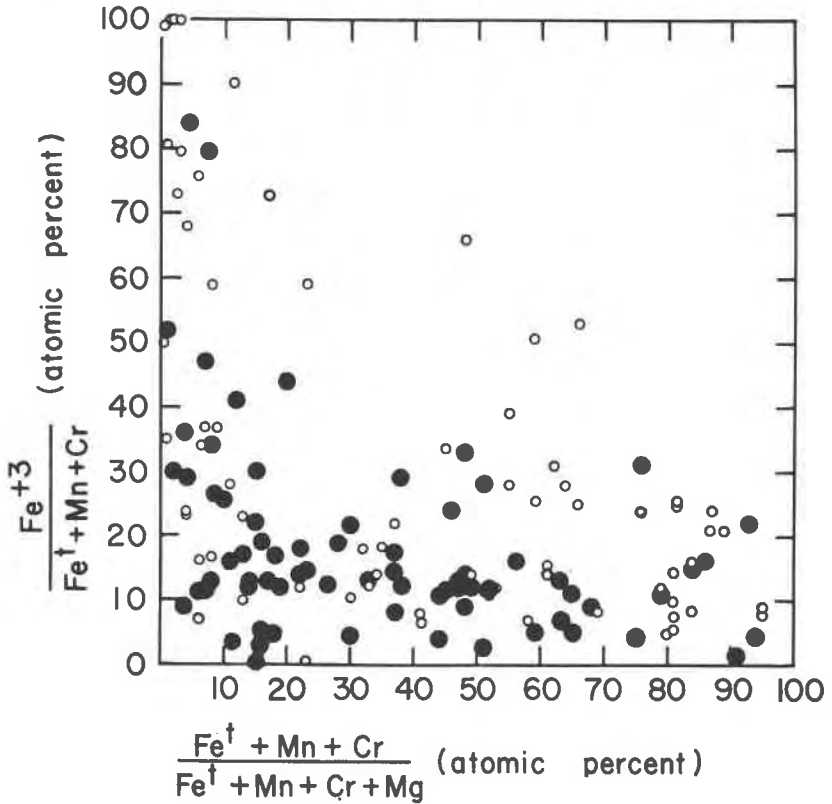


Fig. 3. Relationship between $\text{Fe}^{3+}/\text{Fe}^{2+}+\text{Mn}+\text{Cr}$ and $\text{Fe}^{2+}+\text{Mn}+\text{Cr}/\text{Fe}^{2+}+\text{Mn}+\text{Cr}+\text{Mg}$. Group I analyses—solid dots; Groups II and IIIa—circles.

per cent Cr_2O_3 has little structural effect on chlorite and used 2 per cent by weight as the division between Cr-bearing chlorite and chromium chlorite. Eight analyses of chlorite with $\text{Cr}_2\text{O}_3 > 2$ weight per cent were calculated into atoms per 10 cations. The Al values for these eight analyses are lower than for any other group of chlorites and the Fe values are also low. However, most of these chlorites are associated with ultramafic rock, and low Al and low Fe are also characteristic of other chlorites associated with ultramafic rocks. The reported values for Cr_2O_3 range from 3.27 to 13.46 weight per cent and for NiO from nil to 0.21 weight per cent. The reported Cr_2O_3 values for the other chlorite groups are as follows: Group Ie, 0.00; Group Ib, nil, trace; Group Id, 1.10, 0.86, 1.88, 0.02, Cr 0. X; Group If, 1.0; Group IIc, 0.00, 0.00; Group IIIa 1.14, 0.85, 1.53, 0.10, 0.54, 0.12, and 6 reports of 0.00. Most

of the reported localities for the values given for Group IIIa are localities known for their ultramafic rocks and Group Id is the group associated with ultramafic rock.

Chlorites which contain appreciable Cr_2O_3 are likely to be from ultramafic rocks and to be associated with chromite; they are commonly lavender or rose in color and are commonly low Al and low Fe. Chlorites from other associations do not seem to contain appreciable Cr.

NiO was reported for 17 samples ranging from 0.00–0.28 weight per cent, including 8 reports of 0.00 and 2 reports of trace. F was reported as 0.00 weight per cent in 5 analyses and 0.01 weight per cent in one. Cl was reported as Trace and 0.00; CoO as 0.01; V_2O_3 as 0.06; and As_2O_3 as 0.003 weight per cent. Cu was reported as 0.00, 0.00, 0.006, and Zn as 0.15 weight per cent.

OPTICAL PROPERTIES OF CHLORITE

Chlorite is generally monoclinic, the optic plane parallel to (010) ($\beta \parallel b$) and the acute bisectrix nearly normal to 001. The β refractive index ranges from about 1.56 to about 1.68, the birefringence from 0.00 to about 0.15. In general, higher index chlorites have a negative optic sign, and lower index chlorites have a positive optic sign. The sign of elongation is always opposite that of the optic sign and is easier to obtain in fine-grained chlorites than the optic sign. Near the sign change the mineral becomes sensibly isotropic; across the sign change α and γ vary such that the former α direction becomes γ and vice versa. Pronounced abnormal birefringence near the sign change is a result of the mineral becoming isotropic for part of the spectrum and anisotropic for another part. The low index (the positive sign) side of the sign change exhibits abnormal brown interference colors, whereas the high index (the negative sign) side exhibits abnormal violet or blue interference colors. The birefringence increases with both increasing and decreasing refractive index away from the sign change.

Orcel (1927, p. 417) indicated that the change in optic sign occurs at $\beta \approx 1.631$; Wiseman (1934, p. 362) placed it at 1.632 and Miyashiro (1958, p. 254) at 1.630. Hutton (1940, p. 19) found the sign changed at $\beta = 1.631$ for over 30 chlorites, the β of which ranged from 1.607 to 1.639, from quartz-feldspar schists and greenschists from New Zealand. A. H. Chidester and the author have measured the indices of a large number of chlorites from mica schist, greenstone, amphibolite, and ultramafic bodies from northern Vermont. Thirty-five of these have β between 1.622 and 1.643. The sign changed at β about 1.628; the highest index positive chlorite has $\beta = 1.629$, the lowest index negative chlorite had

$\beta = 1.627$. The β index at which the sign changes in chlorite can be given as 1.630 ± 0.003 , the error usually given for the determination of refractive indices.

Ten chlorites with $\beta < 1.625$ are biaxial negative, rather than having the positive sign suggested by the preceding statement. Five of these are from Group IIe—chlorites from amygdules and veins in mafic igneous rocks. There are 11 chlorites in Group IIe; the locality cited for three others in Group IIIa suggests that they belong to Group IIe; thirteen of these have a negative sign. The structural formulas for a number of the highest quality of these analyses suggests that some Al in six-fold coordination in these chlorites is balanced by H deficiency; it seems possible that the anomalous optic sign is related to this feature.

A very low-index sign change has also been observed in chlorite. Chlorite from serpentinite bodies in northern Vermont change sign at $\beta \approx 1.570$, and the associated antigorite also has a negative sign. Shirozu (1958b) describes a similar aggregate of chlorite with positive sign of elongation and presumably negative sign. Detailed x-ray and DTA studies indicated that it was a mixture of chlorite (14 Å) and aluminian serpentine (7 Å).

CORRELATION BETWEEN OPTICAL PROPERTIES, MINERALOGIC OR GEOLOGIC ASSOCIATION AND $\text{Fe} + \text{Mn} + \text{Cr} / \text{Fe} + \text{Mn} + \text{Cr} + \text{Mg}$

Figure 4 shows the relation between optical properties and $\text{Fe} + \text{Mn} + \text{Cr} / \text{Fe} + \text{Mn} + \text{Cr} + \text{Mg}$ (F/FM) for the 73 chlorites of Groups Ia–If, which include most of the associations in which chlorite would be classed as a rock-forming mineral. The curve for β was fitted by inspection, rather than numerically in order to permit consideration of those analyses for which a range for β is indicated from the optic sign and α and γ . A better fit was achieved with a slight break in slope at $\beta = 1.630$ than by any straight line. The curve fit was checked by independent fitting by several other persons. As discussed in the previous section a sign change occurs at $\beta = 1.630$, at which point $\alpha = \beta = \gamma$ and $(\gamma - \alpha) = 0$. The lines for α and γ were fitted to make $\alpha = \beta = \gamma = 1.630$; this point is at an F/FM value of 52 per cent.

The average deviation of β from the curve for analyses of Groups Ia–If is ± 0.0030 ; average deviations for the individual groups are: Ia $\pm .0038$; Ib $\pm .0027$; Ic $\pm .0006$; Id $\pm .0026$; Ie $\pm .0038$; If $\pm .0032$. There is positive reason to believe that 18 of the Group I samples are of high quality, either because of the published description or of personal knowledge of the sample purity and analytical quality coupled with low K_2O , Na_2O , and CaO values. These 18 samples have an average deviation of only ± 0.0023 .

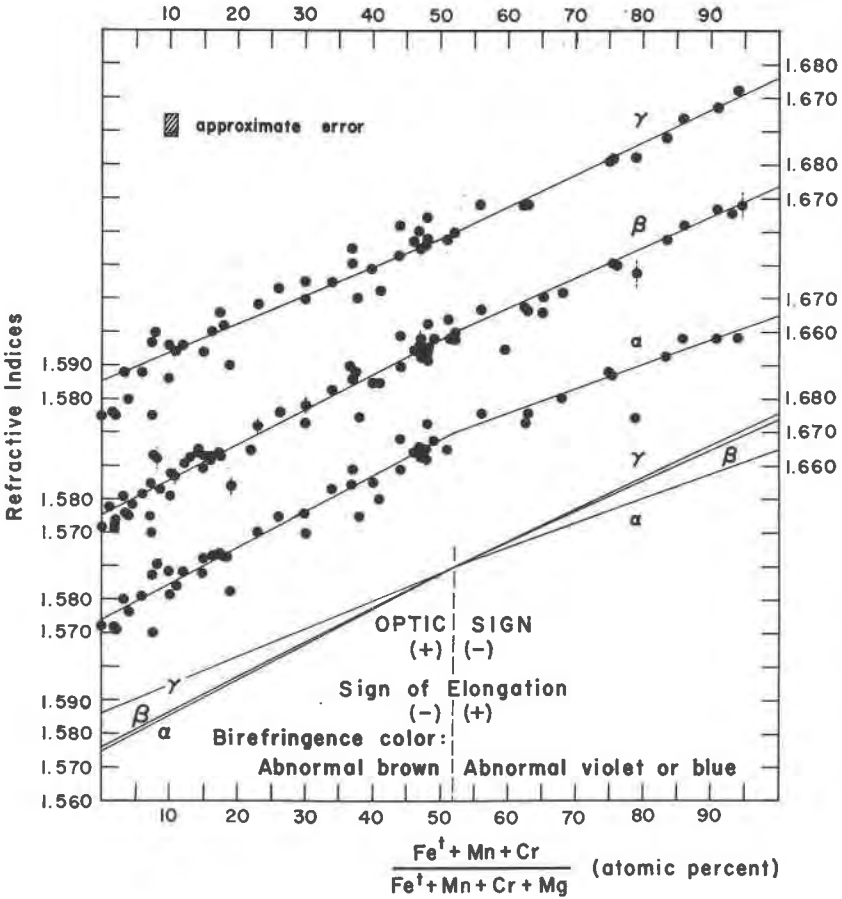


FIG. 4. Correlation between optical properties and $\frac{Fe+Mn+Cr}{Fe+Mn+Cr+Mg}$ for chlorite of Groups Ia-Ii.

Of the 73 samples in these six groups, 82 per cent have a F/FM value which deviates less than 0.05 from the fitted curve for β . The probable errors in chemical analysis and determination of the refractive indices are sufficient to account for much of this deviation. The standard deviation of the "normal" analytical error in F/FM, calculated for a typical analysis of chlorite, is 0.014. Error in the determination of refractive indices is commonly given as ± 0.003 . The platy habit, abnormal interference colors, fine grain size, and color increase the difficulty of measuring all the indices of chlorite precisely. Moreover, these determinations were made by many different workers under many different

conditions, and a range for β was approximated from the other indices for some of these chlorites. Thus, the error in β index for the individual points is at least ± 0.003 , and likely ± 0.004 , for which the fitted curve would give a variation of about ± 0.03 for the F/FM value.

The curve for β also fits the data for Groups IIa–IIc and Group IIIa fairly well, but there is considerably more general deviation and a number of gross deviations. The average deviation of β from the curve is ± 0.0060 . Many of the values for Group IIe—chlorite from amygdules or veins in mafic igneous rock—deviate seriously and systematically as did the optic signs for this group. The β indices average about 0.011 less than the curve would indicate for their F/FM value.

Surprisingly chromium chlorites (Group IIIc) and chlorites associated with Mn-minerals (Group IIIb) also fit the curve very well, but chlorites of Group IIId selected from Serdyuchenko (1953) deviate grossly and, as was suggested earlier, seem to represent inferior data.

The deviation of the individual β 's of Groups Ia–If, IIa–IIe, and IIIa from the fitted curve was plotted against $(\text{Fe}^{3+} + \text{Cr})$, $(\text{Al} + \text{Cr})$, $(\text{Al}^{\text{VI}} + \text{Cr} - \text{Al}^{\text{IV}})$, and $\text{Fe}^{3+}/\text{Fe} + \text{Mn} + \text{Cr}$. No systematic relationship is apparent in any of these diagrams and it seems likely that the deviations are essentially random. It was pointed out earlier that positive $(\text{Al}^{\text{VI}} - \text{Al}^{\text{IV}})$ values correspond to vacancies in the six-fold position for analyses calculated by the normal procedure and that negative $(\text{Al}^{\text{VI}} - \text{Al}^{\text{IV}})$ values as calculated by other procedures correspond to more cations than the available positions. If appreciable vacancies truly occurred it would be expected that they should markedly affect the refractive indices. The fact that no such correlation is apparent suggests that the range in values for $(\text{Al}^{\text{VI}} - \text{Al}^{\text{IV}})$ is not real, but merely the result of poor data.

Although no correlation was detected between $\text{Al} + \text{Cr}$ and β , both Winchell (1936) and Hey (1954) indicate that increasing Al decreases β . Hey derived his diagram from multiple regressions, but a number of apparently good analyses do not fit the diagram at all well. Moreover, the sign change for a medial value of Al (2.7) falls at about 70 per cent $\text{Fe}/\text{Fe} + \text{Mg}$ and an index of about 1.647 as compared to values for the sign change of 52 per cent F/FM and 1.630 for β observed by the author and by numerous other authors cited above.

CORRELATION OF BASAL SPACING, $d(001)$, AND AL CONTENT

Optical properties are of no value for estimating the Al content of chlorite, but a number of workers have shown that the basal spacing decreases with Al content. Recent papers are those by Hey (1954), Brindley and Gillery (1956), Shirozu (1958a, 1960), and Kovalev (1956) on natural chlorites and by Nelson and Roy (1958) on synthetic chlorites.

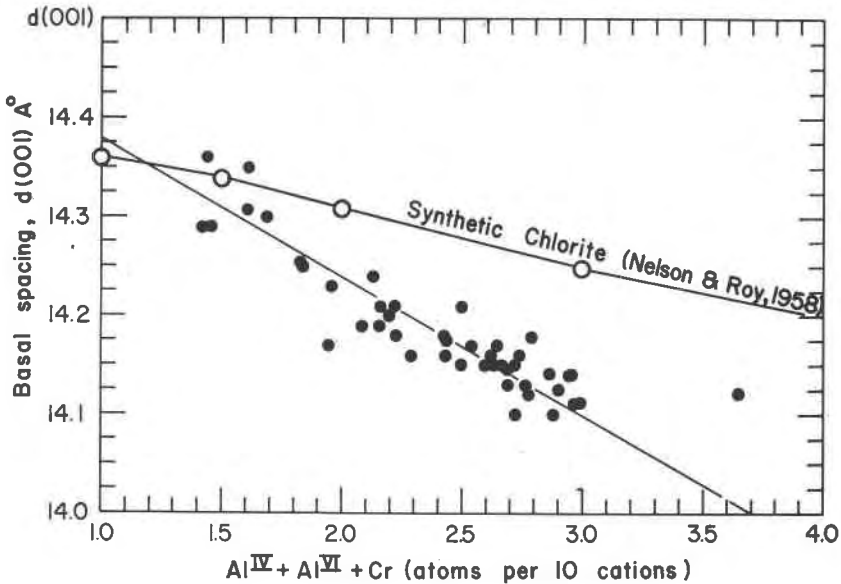


FIG. 5. Relation between basal spacing, $d(100)$, and Al content.

Nearly 90 analyses of chlorites for which basal spacings are available were obtained, but many of these values are not accurate enough to be useful. The relation of basal spacing to Al content with respect to the quality of x -ray data was plotted and it became clear that a reasonable correlation could only be established on basal spacings corrected by means of an internal standard. The values from Phillips (1954), for example, show a similar correlation, but a systematic displacement to smaller basal spacings as compared to data calibrated with an internal standard.

Figure 5 shows the relation for 45 samples between Al content in atoms per 10-cations and basal spacings based on the average of a number of higher-order reflections or a single high-order reflection and corrected by means of an internal standard. Among the analyses recalculated on this basis and included in Fig. 5 are 11 from Shirozu (1958a), 16 from Kovalev (1956), 5 from the author (unpublished) and 5 from the A.S.T.M. file. The equation of the least-squares regression line shown on Fig. 5 is: $y = -7.117x + 103.346$, where $y = d(001)$ Å and $x = \text{Al}^{\text{IV}} + \text{Al}^{\text{VI}} + \text{Cr}$ in atoms per 10 cations. The curve for natural chlorite clearly differs from that for synthetic Mg-chlorite (Nelson and Roy, 1958). No reason is known for the difference, although Gillery (1959, p. 151) has suggested that it might be due to uneven distribution of cations between the two different six-fold layers.

SUMMARY

The structure of chlorite permits extensive isomorphic substitution, and there seem to be no miscibility gaps within the observed range of composition. The composition of chlorite depends upon the total composition of the rock and upon the minerals associated with it. As suggested by a number of recent authors there seems to be no good reason to continue the use of the large number of ill-defined varietal names. In routine petrographic work the optic sign and interference colors may be used to estimate $Fe/Fe+Mg$ for chlorite of most associations. Chlorite with a positive sign and no abnormal interference might reasonably be called Mg-rich chlorite, one with positive sign and abnormal brown interference colors might be called Mg-Fe chlorite, one with negative sign and abnormal blue or violet interference colors might be called Fe-Mg chlorite, and one with negative sign and no abnormal interference colors might be called Fe-rich chlorite.

In more detailed petrographic work the chemical composition of chlorite of most geologic and mineralogic associations may be fairly accurately determined from the refractive indices and the basal spacings. The Al content may be estimated from an accurate determination of the basal spacing; Al is assumed to be equally partitioned between the four- and six-fold positions. The Mg content and the $Fe+Mn+Cr$ content may be estimated from the correlation of β index with $Fe+Mn+Cr/Fe+Mn+Cr+Mg$. In rock-forming chlorite with $Fe+Mn+Cr/Fe+Mn+Cr+Mg > 10$ per cent, Fe^{3+} will constitute about 14 ± 9 per cent of the $Fe+Mn+Cr$; below 10 per cent Fe^{3+} will be a small value. Mn will generally constitute less than 2 per cent of the $Fe+Mn+Cr$ for chlorite not associated with Mn-minerals. Chlorites not associated with ultramafic rocks or with chromite and, in general, chlorites with $Fe+Mn+Cr/Fe+Mn+Cr+Mg > 10$ per cent will not contain appreciable Cr. High Mn-values in chlorite with $Fe+Mn+Cr/Fe+Mn+Cr+Mg < 10$ per cent are likely to be indicated by orange-red colors and high Cr-values by lavender or rose colors.

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REFERENCES

- AHRENS, L. H. (1954), A note on the relationship between the precision of classical methods of rock analysis and the concentration of each constituent. *Mineral. Mag.*, **30**, 467–470.
- BANNISTER, F. A., AND W. F. WHITTARD (1945), A magnesian chamosite from the Wenlock limestone of Wickwar, Gloucestershire. *Mineral. Mag.*, **27**, 99–111.
- BRADLEY, W. F. (1959), Current progress in silicate structures. *Proc. 6th Natl. Conf. Clays and Clay Minerals*, Pergamon Press, 18–25.
- BRINDLEY, G. W. (1951), *X-ray identification and structure of clay minerals*. Mineral. Soc., London.
- (1955), Structural mineralogy of clays. *Proc. 1st Natl. Conf. Clays and Clay Minerals, Calif. Divis. Mines Bull.*, **169**, 33–44.
- AND F. H. GILLERY (1956), *X-ray identification of chlorite species*. *Am. Mineral.*, **41**, 169–187.
- B. M. OUGHTON, AND KEITH ROBINSON (1950), Polymorphism of the chlorites; I, Ordered structures. *Acta. Cryst.*, **3**, 408–415.
- AND R. F. YUELL (1953), Ferric chamosite and ferric chamosite. *Mineral. Mag.*, **30**, 57–70.
- BROWN, GEORGE (1955), The effect of isomorphous substitutions on the intensities of mica and chlorite-type structure. *Mineral. Mag.*, **30**, 657–665.
- DSCHANG, G. L. (1931), Die Beziehungen zwischen chemischer Zusammensetzung und den physikalisch-optischen Eigenschaften in der Chloritgruppe. *Chemie Erde*, **6**, 416–439.
- ENGELHARDT, WOLF VON (1942), Die Strukturen von Thuringit, Bavalit, und Chamosit und ihre Stellung in der Chloritgruppe. *Zeit. Krist.*, **104**, 142–159.
- FAIRBAIRN, H. W. (1953), Precision and accuracy of chemical analyses of silicate rocks. *Geochim. et Cosmochim. Acta.*, **4**, 143–156.
- GARRIDO, J. (1949), Structure cristalline d'une chlorite chromifère. *Soc. Franc. Mineral. Cryst. Bull.*, **72**, 549–570.
- GILLERY, F. H. (1959), *X-ray study of synthetic Mg-Al serpentines and chlorites*. *Am. Mineral.*, **44**, 143–152.
- GRUNER, J. W. (1944), The kaolinite structure of amesite, $(\text{OH}_3)(\text{Mg}, \text{Fe})_4(\text{Al}_2)(\text{Si}_2\text{Al}_2)\text{O}_{10}$, and additional notes on chlorites. *Am. Mineral.*, **29**, 422–430.
- HEY, M. H. (1954), A new review of the chlorites. *Mineral. Mag.*, **30**, 277–292.
- HÖDL, ALFRED (1941), Über Chlorite der Ostalpen; Ein Beitrag zur Systematik der Chlorite. *Neues Jahrb. Min., Beil.-Bd.*, **73**, 1–77.
- HUTTON, C. O. (1940), Metamorphism in the Lake Wakatipu region, Western Otago, New Zealand. *New Zealand Dept. Sci. Indust. Res., Geol. Mem.* **5**.
- KOVALEV, G. A. (1956), *X-ray research on iron-magnesium chlorites*. *Cristallographies*, **5**, 259–268.

- LAPHAM, D. M. (1958), Structural and chemical variation in chromium chlorite. *Am. Mineral.*, **43**, 921-956.
- McMURCHY, R. C. (1934), The crystal structure of chlorite minerals. *Zeit. Krist.*, **88**, 420-432.
- MIKHEEVE, V. I. (1953), Determination of the minerals of the chlorite group by *x*-ray methods. *Mem. Soc. Russe. Mineral.*, **82**, 214-217.
- MIYASHIRO, AKIHO (1958), Regional metamorphism of the Gosaisyo-Takanuki district in the central Abukuma Plateau. *Jour. Fac. Sci., Univ. Tokyo*, **11**, 219-272.
- NELSON, B. W. AND RUSTUM ROY (1954), New data on the composition and identification of chlorites. *Proc. 2nd Natl. Conf. Clays and Clay Minerals, U. S. Natl. Acad. Sci.*, 335-348.
- (1958), Synthesis of chlorites and their structural and chemical composition. *Am. Mineral.*, **43**, 707-725.
- ORCEL, J. (1927), Recherches sur la composition chimique des chlorites. *Soc. Franc. Mineral. Cryst. Bull.* **50**, 75-454.
- , S. CAILLÈRE, AND S. HENIN (1950), Nouvel essai de classification des chlorites. *Mineral. Mag.*, **29**, 329-340.
- PAULING, LINUS (1930), The structure of the chlorites. *U. S. Natl. Acad. Sci. Proc.*, **16**, 578-582.
- PHILLIPS, W. R. (1954), A crystal-chemical classification of the chlorite minerals. Unpubl. Ph.D. thesis, Univ. Utah.
- SERDYUCHENKO, D. P. (1953), Chlorites; their chemical composition and classification. *Trudy Inst. Geol. Nauk*, **140**, *Mineral.-Geochem. Ser.* (no. 14).
- SHIROZU, HARUO (1958a), *X*-ray powder patterns and cell dimensions of some chlorites in Japan with a note on their interference colors. *Mineral. Jour.*, **2**, 209-223.
- (1958b), Aluminian serpentine and associated chlorite from Usagiya, Fukuoka Prefecture, Japan. *Mineral. Jour.*, **2**, 298-310.
- (1960), Determination of the chemical composition of chlorite by the *x*-ray and optical methods. *Rept. Inst. Petrol., Mineral., Econ. Geol., Tohoku Univ.*, **44**, 18-22.
- STEINFINK, HUGO (1958), The crystal structure of chlorite: I, A monoclinic polymorph; II, A triclinic polymorph. *Acta. Cryst.*, **11**, 191-198.
- TUDDENHAM, W. M. AND R. J. P. LYON (1959), Relation of infrared spectra and chemical analysis for some chlorites and related minerals. *Anal. Chem.*, **31**, 377-380.
- TURNOCK, A. C. (1960), Stability range of iron chlorites. *Carnegie Inst. Wash., Year Book*, **59**, 98-103.
- WINCHELL, A. N. (1926), Chlorite as a polycomponent system. *Am. Jour. Sci.*, ser. 5, **11**, 284-300.
- (1936), A third study of chlorite. *Am. Mineral.*, **21**, 642-651.
- WISEMAN, J. D. H. (1934), The central and southwest Highland epidiorites, A study in progressive metamorphism. *Geol. Soc. London, Quart. Jour.*, **90**, 354-417.
- YODER, H. S. (1952), The MgO-Al₂O₃-SiO₂-H₂O system and related metamorphic facies. *Am. Jour. Sci., Bowen Vol.*, 569-627.

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