

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

VOL. 3

MAY, 1928

No. 5

ADDITIONAL NOTES ON CHLORITE

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Since the publication of the writer's discussion¹ of "Chlorite as a Polycomponent System," a monograph on the composition of chlorite² has appeared from the pen of Dr. J. Orcel of the Paris Museum of Natural History. This monumental work is so much more complete than any previous study of the chlorite system that our knowledge of the subject has been increased to an extraordinary extent. For example, all previous work on chlorite furnished only eighteen examples of samples on which optic data were measured on material known to be the same as that which was analyzed, and more than half of these are unsatisfactory because of impure material or for other reasons. Orcel gives eighteen new analyses of chlorite made by modern methods on material very carefully purified and accompanied by optic data in each case. It is obviously important and almost necessary to make use only of analyses of samples whose purity has been demonstrated by microscopic study in order to make real progress in understanding the composition of complex silicates such as chlorite. It is only because such analyses have been very uncommon that others have been used in previous attempts to unravel the problems of the constitution of chlorite. Orcel has added very largely to the stock of new analyses of chlorite of *known purity*, and he has fortunately supplied optic data for nearly all the samples analyzed. Therefore it is desirable to study again the constitution of chlorite and the relations between composition and optic properties.

One chapter of Orcel's monograph, occupying fifty pages, is devoted to a study of the water in chlorites, and particularly to phenomena attending dehydration of various samples of chlorite. Orcel has applied the double galvanometer of Saladin-Le Chatelier

¹ *Am. Jour. Sci.*, CCXI, 1926, pp. 283-300.

² *Recherches sur la Composition Chimiques des Chlorites: Bull. Soc. Min. Fr.*, L, pp. 75-456, 1927; also issued as doctor's thesis No. 1958 (A 1,108) of Univ. Paris, 1927.

to obtain a photographic record of very slight thermal changes in many samples of pure chlorite, including some as different in composition as possible. From this study he reached the extremely important conclusion that Tschermak's theory of the constitution of chlorite is probably incorrect.³ This conclusion is based on the fact that the thermal curves of clinochlorite, ripidolite, penninite, etc., are not like those of antigorite and amésite nor intermediate between them (in character). Such evidence is not at all convincing to the writer especially in view of the fact that the thermal curves obtained by the same method by Orcel on different samples of one kind of chlorite (for example, grochauite, or leuchtenbergite, or ripidolite) differ nearly as much from one another as those of antigorite and of amésite differ from those of clinochlorite and the other intermediate chlorites.

It seemed possible that the new method of studying crystal structure by means of X-ray patterns might throw some light on this question of the relationships between amésite, penninite, antigorite, etc.; consequently patterns were obtained from the following minerals:—

1. Antigorite, Antigorio Valley, Piedmont.
2. Penninite, Viesch, Switzerland.
3. Clinochlorite.
4. Corundophilite, Chester, Mass.
5. Amésite, Chester, Mass.
6. Prochlorite, Vermont.
7. Aphrosiderite, Michigamme, Michigan.
8. Thuringite.

The results, shown in Fig. 1, are not conclusive. The X-ray pattern of antigorite is much simpler than that from any other mineral of the series, a condition which corresponds well with its simpler composition. It has one well-defined line which does not correspond with any line of the aluminous chlorites and is therefore not easily understood. However, it seems to be true that various types of aluminous chlorites differ from one another in their X-ray patterns as much as they differ from antigorite—aside from the simplicity of the latter. It will require a detailed and perhaps prolonged study of these patterns to obtain final results from them.

Although Orcel rejects the theory of Tschermak as improbable, his own classification recognizes a *continuous variation* in composi-

³ *Op. cit.*, p. 288 and 322.

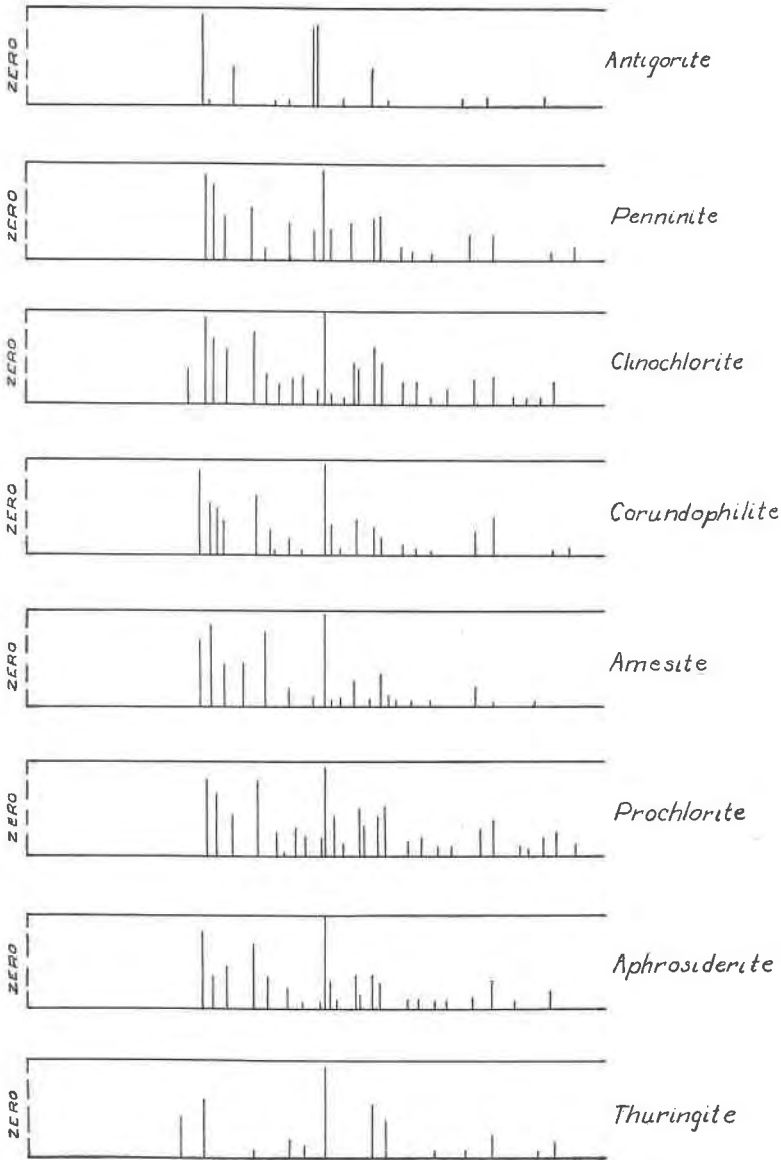


Figure 1. X-ray patterns of antigorite, penninite, clinochlorite, corundophilite, amesite, prochlorite, aphrosiderite and thuringite. The length of each line is proportional to its estimated intensity.

tion from amesite to more than 60 per cent. (apparently to 80 per cent.) of the antigorite molecule.⁴ In any such isomorphous series which is admitted to be continuous, it seems to the writer undesirable and misleading to dignify any definite simple (intermediate) ratio with a special name. Any simple ratio between albite and anorthite in the plagioclase series is exceptional and due merely to chance, and the same kind of statement is true for any isomorphous series. When a simple ratio is the normal result of the natural forces of chemical affinity and crystallization, as in the case of the ratios expressed in the formula of albite, it deserves a special name. When a simple ratio is only a result of chance there is no better reason to give it a special name than there is, for example, to create a series of special names for liquids which consist of mutual solutions of water and alcohol in various simple proportions. If an isomorphous series is sufficiently common and different in its component parts to make special names desirable for its parts, these names should not be supposed to represent simple ratios (which are exceptional), but definite continuous parts of the series, and these parts may well be limited by means of the exceptional simple ratios. These are the ideas which lead the writer to the conclusion that Orcel's new classification of the chlorite system is not acceptable.

It seems reasonable to divide an isomorphous series into parts which represent equal amounts of chemical variation. According to Orcel's classification the differences in composition increase markedly, but irregularly, from penninite to amesite, and there is much less difference in composition between his penninite and clinochlorite than between his corundophilite and amesite. This is doubtless a consequence of attempting to define these types in terms of the accidental simple ratios between SiO_2 and Al_2O_3 .

The new analyses of Orcel have been made by modern methods on samples whose purity has been determined by careful microscopic study. They are therefore very much better than most of the analyses of chlorite published heretofore. It is interesting that these more accurate analyses serve to support the theory of Tschermak since they can be calculated into the Tschermak molecules with discrepancies which are very small and probably negligible in all cases except for those samples containing important

⁴ Orcel expresses this variation not in terms of the amesite and antigorite molecules, but in terms of the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio.

amounts of ferric iron. This is substantially the same condition that was found (allowing larger discrepancies) in the older analyses. Increase in accuracy has resulted in a marked decrease in the discrepancies, exactly as it should if the theory of Tschermak is correct. It is very interesting to observe, also, that Orcel's analyses of chlorites rich in ferric iron do not fit the theory of Tschermak just as many of the older analyses of thuringite, etc., do not fit that theory. However, the new analyses can be made to correspond very well with Tschermak's theory by the same assumption made in regard to the older analyses, that is, that the iron has changed its state of oxidation (actually or apparently) in the chlorite after its formation. In the case of Orcel's analyses it is necessary to assume that the ferric iron has been produced in the chlorites by oxidation of ferrous iron. By assuming that all the ferric iron in all of Orcel's analyses represents oxidized ferrous iron, his analyses can be calculated into Tschermak's molecules with discrepancies which are negligible in all cases.⁵ It is hoped that further attempts to change the state of oxidation of iron in chlorites experimentally may be undertaken soon.

Summarizing the situation produced by the publication of Orcel's new data in regard to the chemical constitution of chlorites it seems to the writer that the evidence in favor of Tschermak's theory has been considerably strengthened and no changes are needed in the chemical interpretation previously presented.⁶

The situation is not the same with regard to the relations between optic properties and variations in chemical composition. Orcel's new data are much better in purity of samples and accuracy of correlation between optic and chemical data than were available before. In fact, if only those analyses be considered which are accompanied by optic data on the same material and which can be calculated into Tschermak's molecules with a maximum discrepancy (disregarding H_2O) of 1.5 per cent. of SiO_2 there were only six such analyses available before the publication of Orcel's monograph; he has added twice as many. Therefore it is now possible to revise the diagram showing the relations between optic properties and chemical composition and make it more accurate. The new data require only one important change in the diagram,

⁵ Disregarding H_2O and calculating so as to concentrate the discrepancies in SiO_2 , the maximum discrepancy is 0.8 SiO_2 .

⁶ A. N. Winchell: *Am. Jour. Sci.*, **CCXI**, 1926, p. 283.

namely, a more rapid increase in the mean index of refraction. It is very gratifying to find that the diagram needs almost no change so far as the optic sign and birefringence are concerned. The revised diagram⁷ is given in Figure 2.

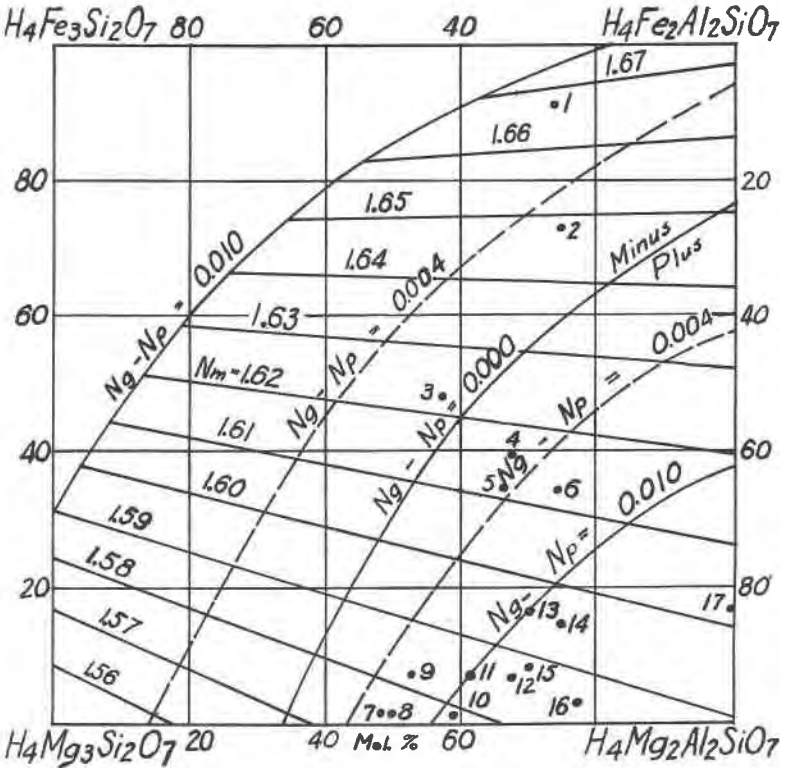


Figure 2. Relations between optic properties and chemical composition in the chlorite system.

It is obvious that this diagram makes it necessary to redefine the optic subdivisions of the chlorite system in order to make them correspond as nearly as possible with the chemical subdivisions. The new statement follows:—

⁷ It is an interesting fact that Jakob's "ekmannite" (*Schweiz. Min. Pet. Mit.*, IV, 1924, p. 51) which seems to be a manganiferous ferroantigorite fits the diagram very well in optic sign and mean birefringence, but has a birefringence of 0.048.

OPTIC SUBDIVISIONS OF THE CHLORITE SYSTEM

NAME	SIGN	N_m	$N_o - N_p$
Antigorite	-	1.55-1.58	0.004-0.010
Delessite	-	1.59-1.61	0.000-0.004
Jenkinsite	-	1.58-1.61	0.004-0.010
Diabantite	-	1.61-1.63	0.000-0.004
Aphrosiderite	-	1.63-1.65	0.000-0.004
Daphnite	-	1.65-1.68	0.000-0.004
Thuringite	-	1.65-1.68	0.004-0.010
Penninite	-	1.56-1.59	0.000-0.004
Penninite	+	1.57-1.61	0.000-0.004
Ripidolite	+	1.61-1.63	0.000-0.004
Clinochlorite	+	1.57-1.59	0.004-0.010
Prochlorite	+	1.59-1.62	0.004-0.010
Amesite	+	1.58-1.61	0.010-0.015 ±

In regard to the accuracy of Fig. 2 it may be noted that the points on the diagram are plotted from the analyses (list of references given later) and the diagram gives the mean index of refraction with a maximum error of 0.007; gives the birefringence with a maximum error of 0.005, except for No. 16 for which the error is 0.008; and gives the optic sign correctly in all cases.

The diagram in its revised form has been based entirely on the most accurate data available, but it is worthy of note that it gives the optic data with reasonable accuracy for many cases,⁸ which have not been used because the optic measures were not made at the same time as the analyses and therefore were not *certainly* made on the same material that was analyzed, and also for the recent analyses of Shannon⁹ and others for which material was too scanty to permit complete analyses.

In the writer's former study of chlorite¹⁰ the conclusion was reached that some chlorite is isotropic and the evidence in support of this conclusion was summarized. Orcel considers the evidence insufficient to prove the point and presents a diagram (Fig. 15, p. 417) showing variations in composition in relation to variations in the mean index of refraction and the birefringence with a change in optic sign without passing through zero birefringence. His diagram is open to two criticisms. First, equal distances on the

⁸ See especially the cases of chlorites analyzed by others and optically measured by Orcel.

⁹ *U. S. Nat. Mus. Bull.*, 131, 1926, p. 378.

¹⁰ *Am. Jour. Sci.*, CCXI, 1926, p. 283.

axis of abscissas do not represent equal differences of composition—on the contrary, the distance from zero to one represents more difference in composition than the entire remaining distance, one to ten; this is the main reason for the sharp curvature in the lines representing optic properties. Second, the diagram shows a change of sign without passing through zero birefringence, which is not

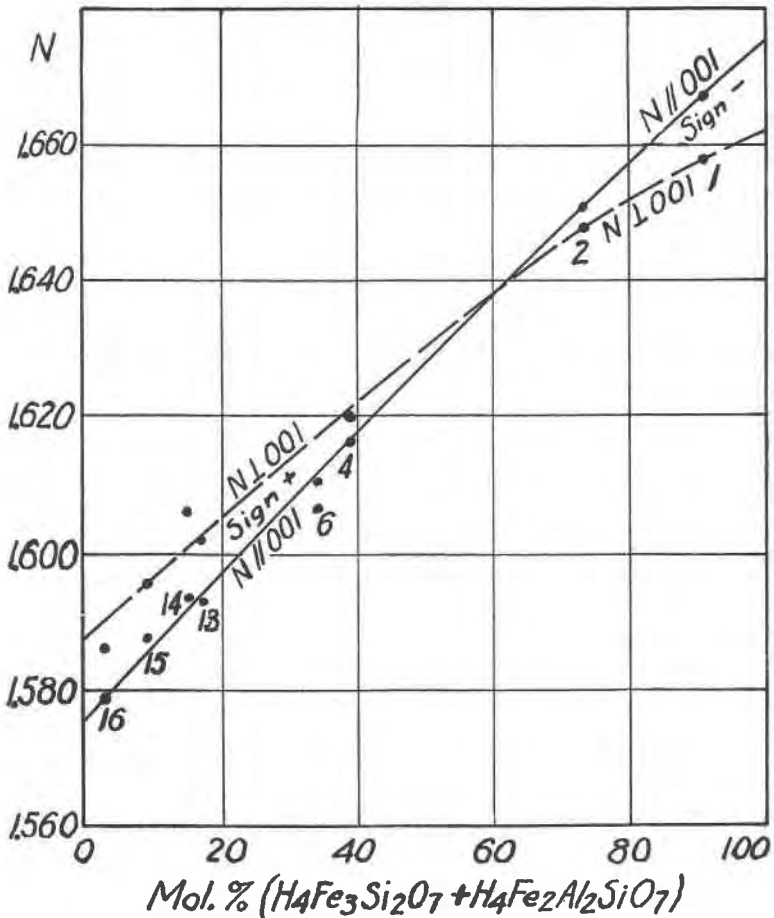


Figure 3. Relations between tenor of ferrous iron molecules and indices of refraction in chlorites containing 68–78 per cent. of (amesite+daphnite). N_0 is abnormally high in No. 14 probably on account of more Fe_2O_3 than in Nos. 13 and 15. The indices of No. 6 are a little too low, but the birefringence is about correct for the diagram.

correct for chlorite, as can be seen from a study of Fig. 3. The index of refraction for the direction normal to 001 is greater than that for directions parallel with 001 for chlorites with little ferrous iron; the difference decreases with increase of ferrous iron; finally, the index for the direction normal to 001 becomes less than that for directions parallel with 001 in chlorites with much ferrous iron. If it be admitted that physical properties in an isomorphous series vary continuously, then it is necessary that in this series of chlorites the two indices must be equal at some point, and chlorite of this type must be isotropic, at least for monochromatic light.

REFERENCES AND OPTIC DATA FOR FIGURES 2 AND 3.

1. "Bavalite," Bas-Vallon, France. J. Orce! : *Bull. Soc. Fr. Min.*, **L**, 1927, pp. 245-248; Orce!'s analysis 128. $G.=3.20$, $(-)2V=\text{very small}$. $N_o=N_m=1.667$ (calc. from N_o-N_p), $N_p=1.658$, $N_o-N_p=0.009$. $X=\text{pale yellowish green}$, $Y=Z=\text{olive-green}$.
2. "Aphrosiderite," Weilburg, Nassau. J. Orce! : *op. cit.*, pp. 251-253; Orce!'s analysis 123. $(-)2V=?$ $N_o=N_m=1.651$, $N_p=1.648$, $N_o-N_p=0.003$ (calc.), 0.004 (obs.). $X=\text{pale yellowish green}$, $Y^{\parallel}=Z=\text{dark olive green}$. These data serve to correct the data of Larsen (*U. S. Geol. Surv. Bull.* **679**, 1921, p. 41) on unanalyzed "aphrosiderite" from the same locality. Sandburger (*N. Jahrb. Min.*, **1850**, p. 341) gives $G.=2.8$ for aphrosiderite of similar composition from the same locality.
3. Diabantite, Westfield, Mass. E. V. Shannon: *Proc. U. S. Nat. Mus.*, **LVII**, 1920, p. 397. $G.=2.77$. $(-)2V=0^{\circ}\pm$. $N=1.62\pm$.
4. "Ripidolite," Isère, France. J. Orce! : *Op. cit.*, pp. 229-231; Orce!'s analysis 95. $G.=2.90$. $(+)2V=\text{very small}$. $N_o=1.620D$, $N_m=N_p=1.616$, $N_o-N_p=0.004$. $Z\perp 001=\text{very small}$. Color olive green very weakly pleochroic with $X=Y>Z$.
5. "Ripidolite," Androta, Madagascar. J. Orce! : *Op. cit.*, pp. 227-229; Orce!'s analysis 93. $G=2.883$ or 2.87 . $(+)2V=0^{\circ}$. $N_o=1.621$, $N_m=N_p=1.618$, $N_o-N_p=0.003$. $Z\perp 001=\text{small}$. $X=Y=\text{olive green}$, $Z=\text{pale olive green}$.
6. "Prochlorite," Waterworks tunnel, D. C. Analysis by F. W. Clarke and E. A. Schneider: *U. S. Geol. Surv. Bull.* **78**, 1891, p. 19. Optic data by E. S. Larsen (*U. S. Geol. Surv. Bull.* **679**, 1920, p. 123): $(+)2V=\text{small}$; $Z\perp 001$; $N_m=1.605$, $N_o-N_p=\text{weak}$. Optic data also by E. V. Shannon (*Proc. U. S. Nat. Mus.*, **LVII**, 1920, p. 475): $(+)2V=\text{very small}$; $N_o=1.610$, $N_m=N_p=1.606$, $N_o-N_p=0.006$; $X=Y=\text{deep blue-green}$, $Z=\text{pale brownish green}$.
7. "Clinochlore," Togoland. J. Orce! : *Op. cit.*, pp. 267-270; Orce!'s analysis 272. $G.=2.657$. $(+)2V=\text{very small}$. $N_o=1.576$ (calc. from N_o-N_p), $N_m=N_p=1.571$, $N_o-N_p=0.0053$. Contains central zone with $N_o-N_p=0.003$. Common twinning on 001. Color green, not pleochroic.
8. "Chromiferous clinochlore," Togoland. J. Orce! : *Op. cit.*, pp. 267-270; Orce!'s analysis 271. $G.=2.675$. $(+)=\text{very small}$. $N_o=1.584$ (calc. from N_o-N_p), $N_m=N_p=1.579$, $N_o-N_p=0.005$. Contains central zone with $N_o-N_p=0.003$. Color violet or pink, not pleochroic.

¹¹ Orce! gives $X=Y$, which must be incorrect, unless the mineral is positive.

9. "Clinochlore," Besofotra, Madagascar. J. Orcel: *Op. cit.*, pp. 266-267; Orcel's analysis 170. $(+)2V=0^\circ$ nearly. $N_g=1.594$ (calc. from N_g-N_p), $N_m=N_p=1.584$, $N_g-N_p=0.010$. $Z \wedge \perp 001$ =small. Color green, not pleochroic.
10. "Leuchtenbergite," Midongy, Madagascar. J. Orcel: *Op. cit.*, pp. 195-199; Orcel's analysis 47. $G.=2.656$. $(+)2V=18^\circ-19^\circ$ Na. $N_g=1.5904$ Na, $N_m=1.5754$ (calc.) $N_p=1.5749$, $N_g-N_p=0.0155$. Colorless. $Z \wedge \perp 001$ =very small.
11. "Prochlorite," Ambatofinandrahana, Madagascar. J. Orcel: *Op. cit.*, pp. 199-202; Orcel's analysis 71. $G.=2.713$. $(+)2V=29^\circ$ D. $N_g=1.5989$, $N_m=1.5887$, $N_p=1.5880$, $N_g-N_p=0.0109$. Color green. $Z \wedge \perp 001$ =small.
12. "Prochlorite," Carter mine, Madison Co., N. C. J. Orcel: *Op. cit.*, pp. 205-209; Orcel's analysis 57. $G.=2.696$. $(+)2V=19^\circ$. $N_g=1.600$ (calc. from N_g-N_p as measured on another sample), N_m nearly= $N_p=1.588$, $N_g-N_p=0.012$ (measured on another sample).
13. "Prochlorite," Rainbow Camp, Leydsdorp, Transvaal. J. Orcel: *Op. cit.*, pp. 212-216; Orcel's analysis 68. $(+)2V$ =small. $N_g=1.602$ (calc. from N_g-N_p), $N_m=N_p=1.593$, $N_g-N_p=0.009$. Color ash green.
14. "Prochlorite," Antohidrano, Madagascar. J. Orcel: *Op. cit.*, pp. 217-220; Orcel's analysis 67. $G.=2.754$. $(+)2V=25^\circ$; $N_g=1.606$ (calc. from N_g-N_p), $N_m=N_p=1.594$, $N_g-N_p=0.012$. Color green. A slightly different analysis is given by A. Lacroix: *Minéral. Madagascar*, III, 1923, p. 297, with $(+)2E=40^\circ$, $N_g=1.595$, $N_m=1.592$, $N_p=1.584$ —these indices require a negative sign.
15. "Prochlorite," Madison Co., N. C. J. Orcel: *Op. cit.*, pp. 205-209; Orcel's analysis 58. $G.=2.718$. Optic data on p. 415: $N_g=1.596$, $N_m=N_p=1.588$, $N_g-N_p=0.008$. Optic data (and slightly different analysis) also given by Orcel in *Comp. Rend.*, CLXXVI, 1923, p. 1231, as follows: $(+)2V=19^\circ$, $N_g=1.587$, $N_m=1.582$, $N_p=1.576$, $N_g-N_p=0.011$. (N_m must be about 1.578 if $2V$, N_g and N_p are correct).
16. "Sheridanite," Comberousse, Savoie, France. J. Orcel: *Op. cit.*, pp. 189-193; Orcel's analysis 31. $G.=2.680$. $(+)2V=12^\circ \pm$ Na. $N_g=1.586$ (calc. from N_g-N_p), $N_m=1.580$, $N_p=1.578$, $N_g-N_p=0.008$. Colorless spherulites. $Z \wedge \perp 001$ =small.
17. "Amesite," Chester, Mass. E. V. Shannon: *Am. Jour. Sci.*, CXCIX, 1920, p. 96. Orcel's analysis 2. $G.=2.77$. $(+)2V$ =very small. $N_g=1.612$, $N_m=N_p=1.597$, $N_g-N_p=0.015$ (calc.), 0.010 (observ.). Color green. $Z \wedge \perp 001$ =very small.