

BIREFRINGENCE-DISPERSION RATIO AS A DIAGNOSTIC¹

A. N. WINCHELL, *Stamford Research Laboratories, American Cyanamid Company, Stamford, Connecticut,*

AND

WARD B. MEEK, *University of Wisconsin, Madison, Wisconsin.*

ABSTRACT

The ratio between the birefringence (B_D) and the dispersion of the birefringence ($B_F - B_C$) is an optical property which is almost unknown, but it is useful in certain cases. For example, a three- (or four-) component system may have physical properties such that "contour" lines for the commonly used physical characters, such as refringence, birefringence, and specific gravity, are all nearly parallel, but the birefringence-dispersion ratio lines are far from parallel with the other lines in some cases. Some examples are given.

In the case of a simple variation in chemical composition of any mineral, like the variation in olivine from Mg_2SiO_4 to Fe_2SiO_4 , a simple diagram showing the relation between variations in composition and variations in physical characters makes it possible to learn the composition by measuring any one of the physical characters included in the diagram. But when the variation in chemical composition is more complex, leading to three (or four) end-members, no diagram can be made which will give the composition by means of measuring one physical property, since any physical property is necessarily the same along some line (or plane) of the diagram. In order to determine the composition by measuring the physical characters in such a case it is necessary to make use of at least two characters which are represented in the diagram by lines which are not parallel; indeed such lines should be (approximately) at right angles to give satisfactory results. In some cases the lines showing the commonly measured physical characters, such as refringence, birefringence, and specific gravity are parallel (or nearly so) in such diagrams. For such cases it is important to find a physical property which varies in such a way as to be represented by lines (nearly) normal to those for one or more of the other physical characters. It seems probable that such a physical character has been found at least for some ternary systems of the carbonates of the divalent metals commonly known as the calcite group. This group has at least six end-members, namely, $CaCO_3$, $MgCO_3$, $FeCO_3$, $MnCO_3$, $ZnCO_3$, and $CoCO_3$ but so little is known about the properties of $CoCO_3$ that it will not be considered further.

Calcite is found so often in very pure well-formed crystals that its properties have been measured with unusual accuracy. They may be

¹ This article in its present form was written by the senior author, but it is based in large part upon an unpublished article written by the junior author when he was a graduate student at the University of Wisconsin in 1937.

summarized as follows:² $G = 2.71(5)$

$\lambda = 656(C)$	$589(D)$	$486(F)$
$N_O = 1.65440$	1.65835	1.66783
$N_E = 1.48457$	1.48639	1.49074
<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
$N_O - N_E = .16983$	$.17196$	$.17709$

Accordingly, the birefringence for the Na line (or B_{Na}) is 0.17196 and the dispersion of the birefringence, that is, the difference between the birefringence for the F line and that for the C lines, is: $B_F - B_C = .00726$. The ratio between these values {that is $B_{Na} \div (B_F - B_C)$ } is 23.7. Since $B_F - B_C$ is the dispersion (D), $B_{Na} \div (B_F - B_C)$ may be shortened to B/D for convenience. This ratio between the birefringence and the dispersion of the birefringence is the physical property which seems to be useful in some cases.

From other excellent measurements^{2a} of the refringence of calcite it is reasonable to conclude that B/D varies from 23.3 to 24.7, doubtless because of small variations in the composition, such as the presence of small amounts of Mg, Fe, or Mn, proxying for Ca.

Dolomite, $CaMg_2C_2O_6$, nearly always contains more or less Fe, Mn, and excess Ca, which proxy for Mg, therefore its properties vary considerably. According to recent data³ believed to be accurate the magnesian end-member has the following properties: $G = 2.869$.

$\lambda = 656(C)$	$589(D)$	$486(F)$
$N_O = 1.67610$	1.68005	1.68901
$N_E = 1.49950$	1.50125	1.50550
<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
$N_O - N_E = .17660$	$.17880$	$.18351$
$\text{Therefore } B_F - B_C = 0.00691 \text{ and } B/D = 27.3$		

A careful study of siderite from Cornwall⁴ containing 97.5 mol. per cent of $FeCO_3$ and only 1.8% $MnCO_3$, 0.5 $MgCO_3$, and 0.2 $CaCO_3$ gave the following results for Li, Na, and Tl light: $G = 3.937$.

<i>For prism 1</i>			<i>For prism 1a</i>		
$\lambda = 671(Li)$	$589(D)$	$535(Tl)$	$\lambda = 671(Li)$	$589(D)$	$535(Tl)$
$N_O = 1.8649$	1.8734	1.8809	$N_O = 1.8655$	1.8733	1.8812
$N_E = 1.6297$	1.6333	1.6373	$N_E = 1.6306$	1.6342	1.6377
<i>For prism 2</i>			<i>For prism 3</i>		
$\lambda = 671(Li)$	$589(D)$	$535(Tl)$	$\lambda = 671(Li)$	$589(D)$	$535(Tl)$
$N_O = 1.8643$	1.8724	1.8799	$N_O = 1.8642$	1.8722	1.8798
$N_E = 1.6299$	1.6338	1.6371	$N_E = 1.6278$	1.6310	1.6344

² Gifford, J. W., *Proc. Roy. Soc. London*, **70**, 336 (1902).

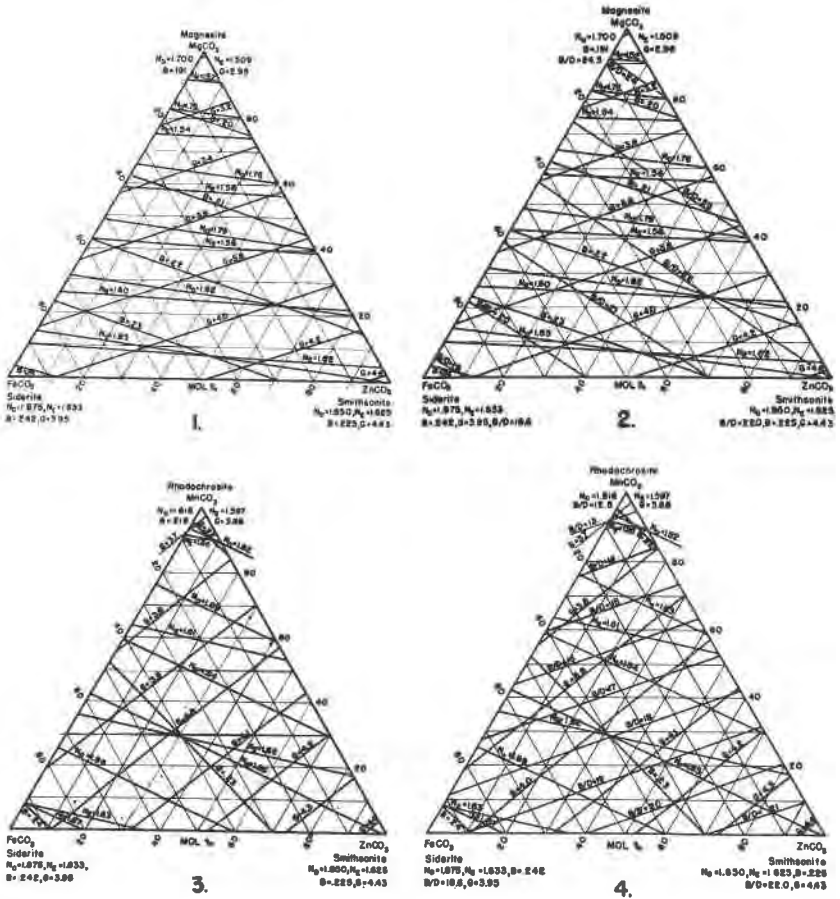
^{2a} See those of Sarasin: *Zeit. Kryst.*, **9**, 605 (1883); Schrauf: *Zeit. Kryst.*, **11**, 20, 674 (1885); Mülheims: *Zeit. Kryst.*, **14**, 224 (1888) and Martens: *Ann. Phys.*, (4) **6**, 603 (1901).

³ Gübelin, E.: *Schw. Min. Pet. Mit.*, **19**, 325 (1940).

⁴ Hutchinson, A.: *Mineral. Mag.*, **13**, 209 (1903).

From these data the indices for C and F light can be obtained by using the Hartmann dispersion net, with the following results:

Prism	1	1a	2	3	Average
B - B _C =	0.0125	0.0132	0.0128	0.0132	0.0128
B/D =	19.2	18.1	18.6	18.3	18.6



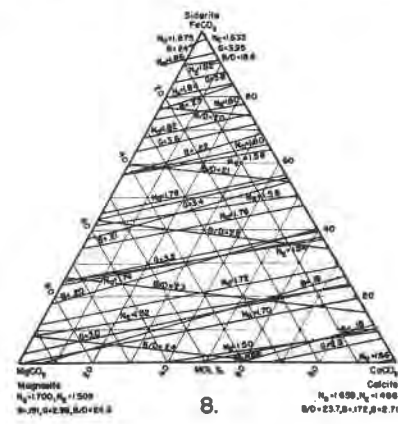
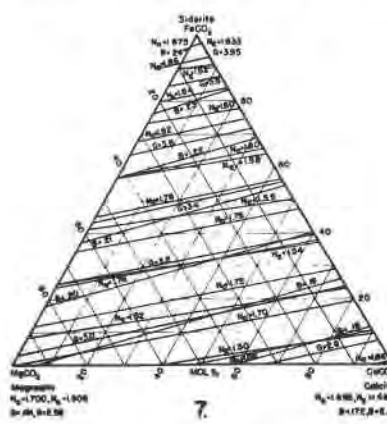
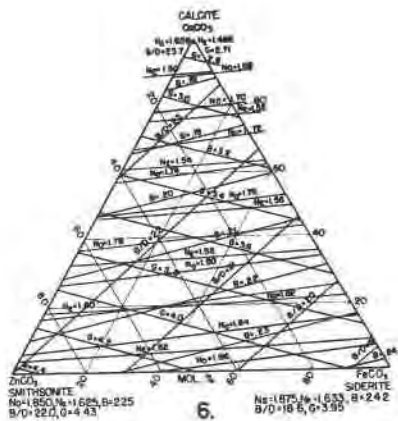
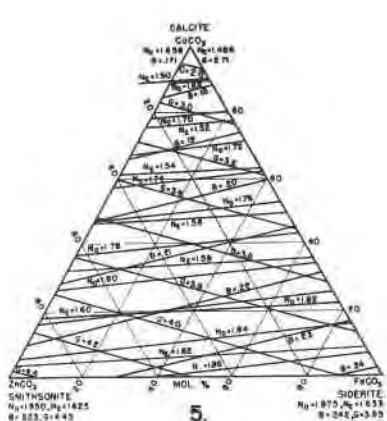
FIGS. 1, 2. Properties of MgCO₃-FeCO₃-ZnCO₃ without (1) and with (2) B/D lines.
 FIGS. 3, 4. Properties of MnCO₃-FeCO₃-ZnCO₃ without (3) and with (4) B/D lines.

The only available data on the dispersion of rhodochrosite are derived from measurements⁵ of the indices of a crystal⁶ from Alma, Park County, Colorado, as follows:

⁵ Made by W. B. Meek by the double variation method (with extrapolation for the O ray).

⁶ Sundius, N. (*Geol. För. Förh. Stockholm*, 47, 269 1925) gives the following analysis of crystals from the same locality: Mol. % MnCO₃ 97.83, FeCO₃ 1.60, MgCO₃ 0.58.

$\lambda=656(C) \quad 589(D) \quad 486(F)$
 $N_O=1.7981 \quad 1.8058 \quad 1.8245$
 $N_E=1.5936 \quad 1.5964 \quad 1.6032$
 $N_O-N_E=0.2045 \quad 0.2094 \quad 0.2213$
 Therefore $B_F-B_C=0.0168$ and $B/D=12.5$



FIGS. 5, 6. Properties of $CaCO_3-ZnCO_3-FeCO_3$ without (5) and with (6) B/D lines.
 FIGS. 7, 8. Properties of $FeCO_3-MgCO_3-CaCO_3$ without (7) and with (8) B/D lines.

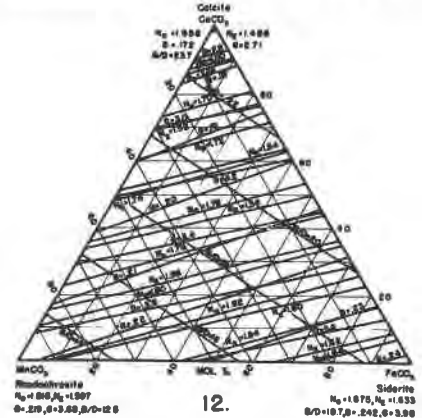
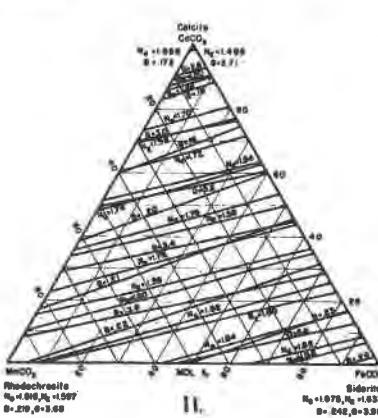
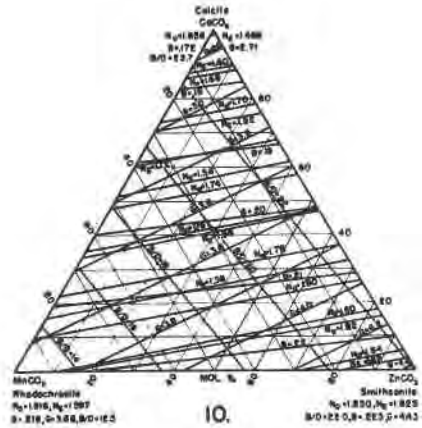
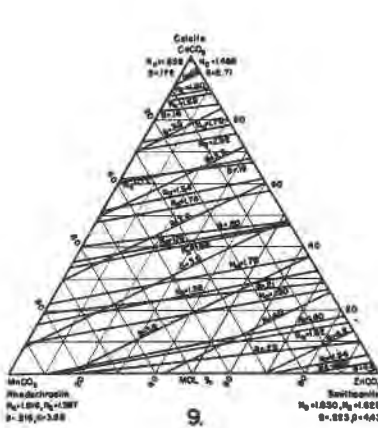
A detailed study of smithsonite from Rhodesia containing 97.0 mol. per cent of $ZnCO_3$ and only 1.4 $MgCO_3$, 1.0 $FeCO_3$ and 0.6 $CaCO_3$ gave the following results:⁷ $G=4.398$.

$\lambda=671(Li) \quad 656(C) \quad 589(D) \quad 535(Tl) \quad 486(F)$
 $N_O=1.8423 \quad 1.8433 \quad 1.8485 \quad 1.8547 \quad 1.8621$
 $N_E=1.6186 \quad 1.6189 \quad 1.6212 \quad 1.6239 \quad 1.6274$
 $N_O-N_E=0.2237 \quad 0.2244 \quad 0.2273 \quad 0.2308 \quad 0.2347$
 Therefore $B_F-B_C=0.0103$ and $B/D=22.0$

⁷ Mountain, E. D.: *Mineral. Mag.*, **21**, 51 (1926).

An unanalyzed sample of smithsonite studied by R. C. Emmons and E. F. Williams⁸ gave the following data, as measured by W. B. Meek:

$\lambda = 656(C)$	589(D)	486(F)
$N_O = 1.8418$	1.8475	1.8614
$N_E = 1.6188$	1.6213	1.6276
$N_O - N_E = 0.2230$	0.2262	0.2338
Therefore $B_F - B_C = 0.0108$ and $B/D = 20.94$		



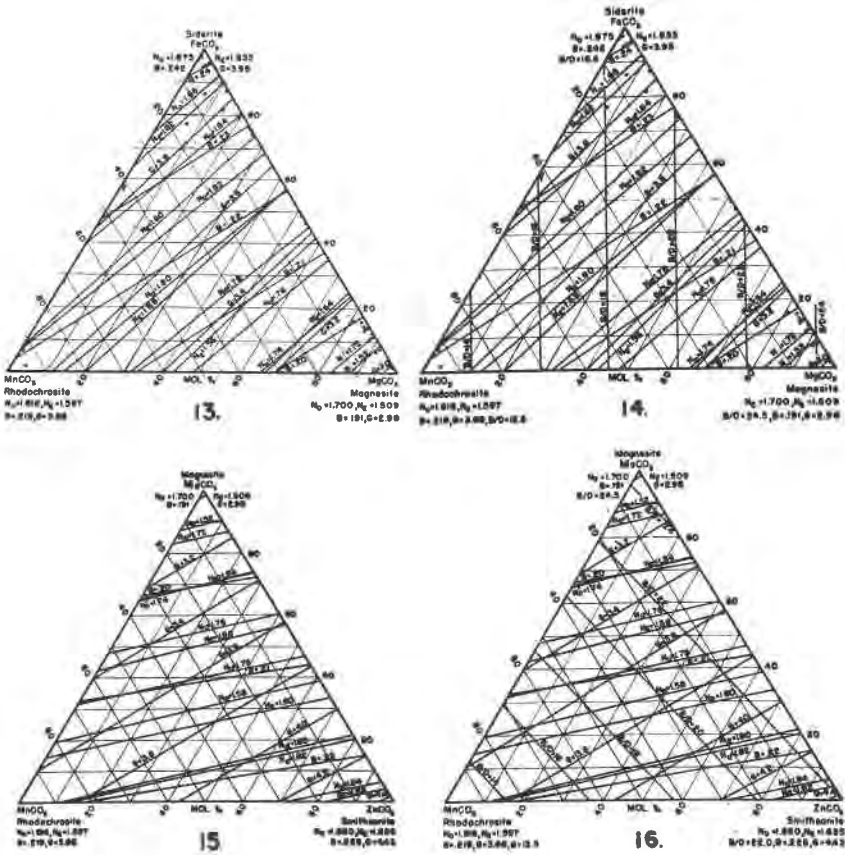
FIGS. 9, 10. Properties of $\text{CaCO}_3\text{-MnCO}_3\text{-ZnCO}_3$ without (9) and with (10) B/D lines.
 FIGS. 11, 12. Properties of $\text{CaCO}_3\text{-MnCO}_3\text{-FeCO}_3$ without (11) and with (12) B/D lines.

Almost the only published data on the dispersion of magnesite are for a crystal from Greiner,⁹ analysis of which gave 74.8 mol % MgCO_3 , 13.4 FeCO_3 , 10.6 MnCO_3 , and 1.2 CaCO_3 ; its refractive indices were found to be:

⁸ Emmons, R. C., and Williams, E. F.: *Jour. Sed. Petrol.*, 4, 32 (1934).

⁹ Eisenhut, K.: *Zeit. Kryst.*, 35, 595 (1901).

$\lambda=671(\text{Li})$	589(D)	535(Tl)
$N_O=1.7118$	1.7174	1.7215
$N_E=1.5263$	1.5285	1.5304
$N_O-N_E=0.1855$	0.1889	0.1911



FIGS. 13, 14. Properties of FeCO₃-MnCO₃-MgCO₃ without (13) and with (14) B/D lines.

FIGS. 15, 16. Properties of MgCO₃-MnCO₃-ZnCO₃ without (15) and with (16) B/D lines.

These figures do not give straight lines on the Hartmann net, but, using Li and Tl to fix the straight lines, the indices for C and F are: $N_O=1.7126$ C, 1.7272 F and $N_E=1.5267$ C, 1.5329 F; therefore $B_F-B_C=0.0084$ and $B/D=22.5$. By making suitable allowance for the effects of Fe, Mn, and Ca, B/D for pure MgCO₃ is 24.5.

The following table summarizes the available data for the calcite group.

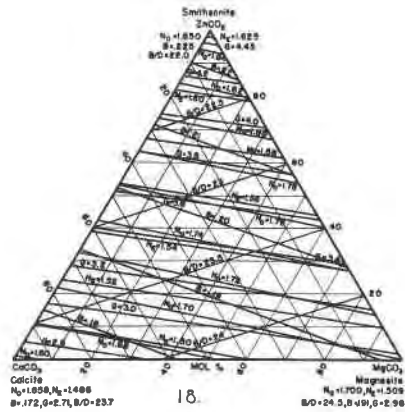
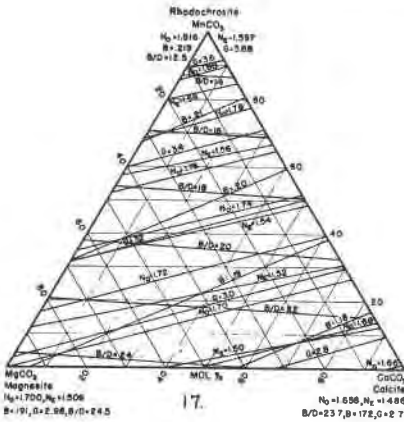


FIG. 17. Properties of MnCO₃-MgCO₃-CaCO₃.
 FIG. 18. Properties of ZnCO₃-CaCO₃-MgCO₃.

	N ₀ (D)	N _E (D)	B _D	B _F -B _C	B/D	G
Calcite	1.65835	1.48639	0.17196	0.00726	23.7	2.71 (5)
Dolomite	1.68005	1.50125	0.17880	0.00691	27.3	2.87
Magnesite { meas. pure MgCO ₃	1.7174	1.5285	0.1889	0.0084	22.5	
	1.700	1.509	0.191		24.5	2.98
Siderite { meas. pure FeCO ₃	1.8734	1.6331	0.2403	0.0128	18.6	3.937
	1.875	1.633+	0.242		18.6	3.95
Rhodochrosite	1.8058	1.5964	0.2094	0.00168	12.5	3.68
Smithsonite { meas. pure ZnCO ₃	1.8485	1.6212	0.2273	0.0103	22.0	4.398
	1.850	0.625 ±	0.225 ±		22.0	4.43

These are the best data at present available, but unfortunately they are not very accurate, except in the case of calcite and dolomite. Of course dolomite is not strictly a member of the calcite group. The remaining five compounds yield ten ternary systems; the refringence, birefringence and density of eight of these are shown in Figures 1, 3, 5, 7, 9, 11, 13 and 15. It is easily seen that in most of these systems the ordinary properties give lines which are nearly parallel; in only two cases (Figs. 1 and 3) are the lines at an angle great enough to give the composition fairly well. The same eight ternary systems are shown in Figures 2, 4, 6, 8, 10, 12, 14, and 16 in which lines for the birefringence dispersion ratio (B/D) have

been added. It is obvious that these lines aid materially in the determination of the composition, especially in the case of $\text{CaCO}_3\text{-ZnCO}_3\text{-FeCO}_3$, $\text{CaCO}_3\text{-MnCO}_3\text{-ZnCO}_3$, $\text{CaCO}_3\text{-MnCO}_3\text{-FeCO}_3$, $\text{FeCO}_3\text{-MnCO}_3\text{-MgCO}_3$, and $\text{MgCO}_3\text{-MnCO}_3\text{-ZnCO}_3$. Figures 17 and 18 show that the same is true for the systems $\text{MnCO}_3\text{-MgCO}_3\text{-CaCO}_3$ and $\text{ZnCO}_3\text{-CaCO}_3\text{-MgCO}_3$. However, it is well known that six ternary systems of the calcite group which have CaCO_3 as one member are not continuous. Of the four others the composition of any mix-crystal can be determined rather well in two cases (Figs. 1 and 3) without using the new diagnostic. In the case of $\text{FeCO}_3\text{-MnCO}_3\text{-MgCO}_3$ and $\text{MgCO}_3\text{-MnCO}_3\text{-ZnCO}_3$, the use of the birefringence-dispersion ratio lines is very helpful, as shown in Figures 13-16.