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REGRESSIONS OF PHYSICAL PROPERTIES ON THE COMPOSITION OF CLINOPYROXENES, PARTS III, IV, AND V

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PART III. THE COMMON SODA-FREE ALUMINA-FREE CLINOPYROXENES

ABSTRACT. Available evidence suggests that the conventional trapezoidal diagram (part of the triangle $Ca_2Si_2O_6$–$Mg_2Si_2O_6$–$Fe_2Si_2O_6$, with the Ca-corner removed) should be considered as a projection of one end and one side of a trigonal prism or tentlike body because in the clinopyroxene formula ABC_2O_6 the cations in position A are normally Ca-sized, and the cations in position B are normally Mg-sized and have correspondingly different effects on physical properties. In this context, clinohypersthene should be $FeMgSi_2O_6$, not $MgFeSi_2O_6$, and slight breaks are expected where the contour lines cross from the triangular field $(Ca,Fe,Mg)MgSi_2O_6$ into the square-, or paralleleogram-shaped field $(Ca,Fe)(Mg,Fe)Si_2O_6$. New diagrams showing the optical properties and specific gravity throughout these fields, based upon recently published regression formulas, are believed to be the best now available for the common soda-free, alumina-free clinopyroxenes. Allowance for other components may be made easily by means of the regressions.

Most internal evidence in the data on optics and specific gravity of these clinopyroxenes does not clearly distinguish between possible states of disorder of Mg and Fe. Nevertheless, one may have a very high statistical confidence that the regression coefficients show that certain cations have significantly different effects on physical properties, depending upon whether they enter the clinopyroxene in position A or B or C of ABC_2O_6, and this is itself evidence of ordered distribution of cations.

INTRODUCTION

In Parts I and II of this series (Winchell and Tilling, 1960; Winchell, 1961), published data on physical properties of clinopyroxenes were studied by means of regression equations. From 155 specimens selected partly for coverage of the clinopyroxene field and partly for adequate accuracy of data reported, the regression constants of optical parameters and specific gravity were obtained in terms of 12 different common chemical replacements of the constituents in diopside. The resulting regression constants were tabulated with their

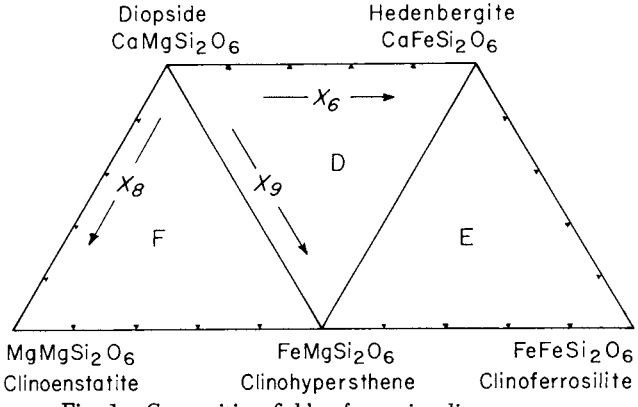

Fig. 1. Composition fields of certain clinopyroxenes.

respective standard deviations and other data in table 4.[1] The constants that concern the optics of common soda-free, alumina-free clinopyroxenes are used in equations (1) through (5) in table 7, herewith. These probably give the best estimates now available for the properties corresponding to all points in the conventional trapezoidal diagram, figure 1, with diopside, hedenbergite, clinoenstatite, clinohypersthene ($FeMgSi_2O_6$), and clinoferrosilite for its principal components. Coefficients b_{ip} for additional terms to be added to the equations in table 7 are given in table 4; such terms should be used, for they permit allowance to be made for aluminum, titanium, ferric iron, manganese, sodium, and potassium, as described in Part II.

TABLE 7

Regression equations for certain physical properties of the common soda-free, alumina-free clinopyroxenes $ABSi_2O_6$ based on coefficients from table 4

		Diopside		Fe″(B)		Mg(A)		Fe″(A)	P
ABC_2O_6	=	$CaMgSi_2O_6$		$CaFeSi_2O_6$		$Mg\,MgSi_2O_6$		$FeMgSi_2O_6$	
"n_x"*	=	1.6658	+	0.0602 x_6	−	0.0155 x_8	+	0.0431 x_9	(1)
"n_y"*	=	1.6720	+	0.0598 x_6	−	0.0236 x_8	+	0.0359 x_9	(2)
n_z	=	1.6946	+	0.0606 x_6	−	0.0341 x_8	+	0.0424 x_9	(3)
Z/c	=	39.9°	+	2.7 x_6	−	17.5 x_8	+	1.5 x_9	(4)
G	=	3.261	+	0.278 x_6	−	0.052 x_8	+	0.258 x_9	(5)
n_z − "n_x"	=	0.0288	+	0.0004 x_6	−	0.0186 x_8	−	0.0007 x_9	(3-1)

* "n_x" is the minimum index for light vibrating parallel to (010); "n_y" is the index for light vibrating parallel to the axis b; hence the birefringence in equation (3-1) is that for sections parallel to (010); it is $n_z - n_x$ for most compositions, but $n_z - n_y$ for compositions near the clinoenstatite-clinohypersthene-clinoferrosilite series.

For example, replacement by Al of 0.04 Si in position C and 0.04 Mg in position B of the formula $ABC_2O_6 = CaMgSi_2O_6$ would increase "n_x", the smallest index of refraction in section parallel to (010), by (.04) (+.0460 −.0341) = .000476, according to the first (p = 1) regression described in Part II. Table 4 contains the regression constants for estimating that the same substitution would also *de*crease "n_y" by (.04) (.0098) = .000392, and n_z by .001308.

Equation (3-1) in table 7 is the difference of equations (3) and (1), and its standard error must therefore be about 1.41 times that of equations (3) and (1). Throughout these studies, the refractive index "n_x" is the lowest index for light vibrating parallel to (010), and "n_y" is the index for light vibrating parallel to b. The column headings in table 7 indicate that the constant terms of the equations represent physical properties of diopside, $CaMgSi_2O_6$; terms in x_6 allow for the substitution of Fe″ for Mg in position B of ABC_2O_6; those in x_8, for substitution of Mg for Ca in A, and those in x_9, for substitution of Fe″ for Ca in A. The subscripts are the same as in Part II.

[1] Tables 1 through 6 referred to in this article are tables 1 through 6 of Part II (Winchell, 1961); the first table in the present pages is table 7.

HYPOTHESIS OF ORDERED CATION DISTRIBUTION

In recalculating analyses to agree with the formula ABC_2O_6, the smallest ions (Si) were assigned to position C; C was then filled up to exactly two cations per six oxygens with the next smallest (Al), and if necessary the next (Fe‴) and the next (Ti); excess of Al, Fe‴, and Ti goes into B, followed by Mg, Fe″, Mn, and very rarely Ca, to fill this space exactly; all remaining cations go into A. This scheme results in assigning Mg first to position B until there is no more room there, and only then to position A; Fe″ can be assigned to position B only after all the Mg is used up without filling that space. These conditions define the "ordered" distribution of Mg and Fe″. A "disordered" condition can be defined on the other hand by combining all Mg and Fe″, and treating this mixture as a single component to be assigned to the positions B and A. In that case, the ratio of Fe″ to Mg is the same in positions A and B. Intermediate conditions between order and disorder are definable similarly. [An "anti-ordered" distribution can also be imagined, in which the crystallographic roles of Mg and Fe are transposed; there is no evidence that this mathematical extrapolation can have any physical reality.] In the only available precise crystal-structure studies (Morimoto, Appleman, and Evans, 1959, 1960; Ghose, 1960), the observed arrangement of cations was fully ordered.

CONVENTIONAL CLINOPYROXENE DIAGRAM

In the conventional diagram representing the compositions of the ordinary soda-poor, alumina-poor clinopyroxenes (fig. 1) there are important consequences of the assumption of ordered cation distribution. The diagram may be divided into three fields, D, E, and F, by boundary lines from clinohypersthene, $FeMgSi_2O_6$, to diopside and to hedenbergite. There is no distinction between the triangular parts D and E of the parallelogram DE, for the amount of Mg replaced by Fe″ in B determines one coordinate x_6, and the amount of Fe″ replacing Ca determines the other coordinate x_9. This parallelogram is thus a distortion of a conventional square diagram representing the system Ca.Fe)-(Mg,Fe)Si_2O_6. If there are other components in B, the coordinate x_6 as here defined is exactly the amount of Fe″, but in more conventional discussions such as that of Hess (1949), the anologous coordinate is usually the total Fe″ + Mn + Fe‴ in that position. Points in the remaining triangle F, figure 1, are de-

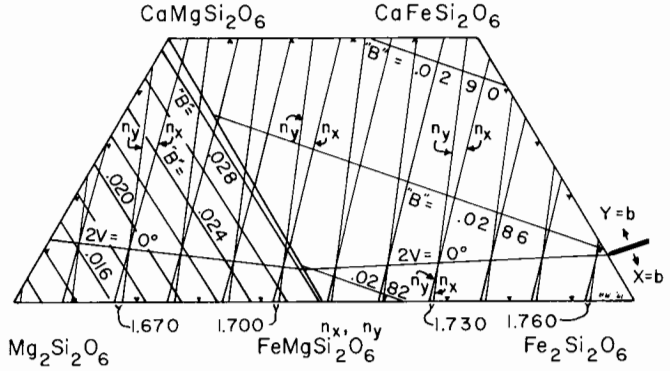

Fig. 2. Clinopyroxene—n_x, n_y, and "B" = n_z − "n_x".

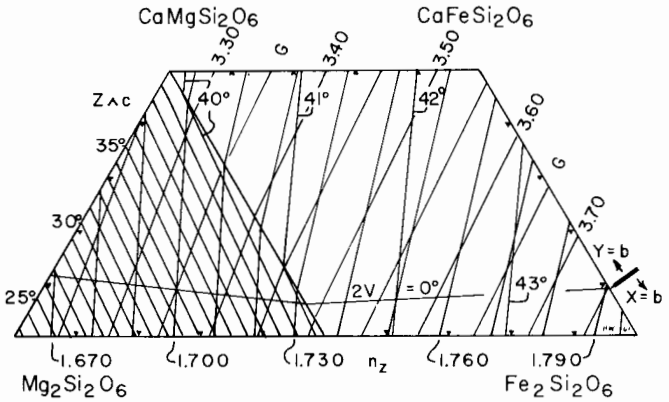

Fig. 3. Clinopyroxene—n_z, Z∧c, and G.

termined by the coordinates x_8 = Mg in position A, and x_9, already defined. This change of coordinate axes is essential as long as we distinguish Mg in position A from Mg in position B, a distinction that seems justified empirically by the few structure determinations cited above and by the regression results in Part II, as well as theoretically by crystal-chemical considerations. The hypothesis of ordered distribution requires that either x_6 or x_8 must always be zero, i.e., that their product is zero.

Because chemical variations within triangle F and parallelogram DE are different in kind, changes of the slopes of contour lines representing physical properties are not only permissible but rather probable along the boundary between DE and F. Because the parallelogram DE is essentially a distorted square diagram, however, no such change is expected along its diagonal.

PHYSICAL PROPERTIES SHOWN ON CONVENTIONAL DIAGRAM

Table 5 gives the optical properties and specific gravity for the four corners and for the midpoints of the upper and lower bases of figure 1. Figures 2 and 3 can be constructed by linear interpolation from these data. The "salite" (162 in table 5) has, as expected, the average of the properties of diopside (156) and hedenbergite (157), but the "clinohypersthene" ($FeMgSi_2O_6$, No. 159) has *not* the average properties of clinoenstatite (158) and clinoferrosilite (171),[2] because of the underlying assumption of ordered distribution of cations in positions A and B. Assuming such ordered distribution, figures 2 and 3 probably represent the best information now available on the optics and specific gravity of the common soda-free and alumina-free clinopyroxenes. As explained above, further replacements of various cations such as Ca by Mn, MgSi by AlAl, etc., can be allowed for by means of small additive corrections derived from the regression equations whose coefficients are listed in table 4.

POSSIBLE DISORDER

Hess (1952) and Hori (1956) established the existence of small optical differences between "orthopyroxenes of the Bushveld type" [slowly cooled] and other orthopyroxenes. Their results showed that cooling history [presum-

[2] In table 5, under clinoferrosilite (171), 1.8867 opposite n_z should read 1.7976.

ably causing order-disorder variations] affects the optical properties in certain cases. In clinopyroxene, a partly disordered arrangement with small amounts of Mg from position A exchanged for Fe″ from position B would seem probable in specimens formed or equilibrated at high temperature and then quenched. If such partially disordered specimens exist, they should occur in thin lava flows. Two-dimensional diagrams like figures 1—3 are not suitable for showing the physical properties for all compositions *and* degrees of disorder. Figure 1, indeed, may be considered as a projection of one side and one end of the tent-shaped solid shown in figure 4. The twisted surface, shaded in the figure, that passes through the corners diopside, hedenbergite, clinoenstatite, and clinoferrosilite, is the locus of all compositions that are fully disordered with respect to the distribution of Fe″ and Mg in A and B. No Mg/Fe″-disorder is definable for compositions on three of the edges of this surface. The hypothetical "anti-ordered" condition may be represented by point A in figure 4, but as already noted, its physical existence would be very improbable if not impossible. To some extent, it is likely that the regression equations, including those in table 7, are applicable for the prediction of properties of disordered specimens, for these equations do show separately the effects of Fe″, for example, in positions A and B; and no significant interaction is likely between cations in A and cations in B. The data on which these equations are based do not include information about the possible state of order or disorder, and the equations are therefore strictly not applicable to the problem of estimating degree of order; nevertheless, if we can use degree of order to separate several specimens in a relatively sensitive composition-region into two groups, then residual errors of prediction may fall into corresponding groups. If so, they afford an indication of the need for an additional regression coefficient related to the degree of order (or to temperature of crystallization or equilibration). An order-parameter can be defined as w in the following formula:

$$(Fe_{\frac{1+w}{2}}Mg_{\frac{1-w}{2}})\,(Mg_{\frac{1+w}{2}}Fe_{\frac{1-w}{2}})\,Si_2O_6.$$

The quantity w is +1 for the ordered, 0 for the disordered, and –1 for the "anti-ordered" condition. Only positive values of w are physically significant.

Figure 5 shows the properties predicted by equations (1) to (5) for a series of clinohypersthenes from the ordered form, $FeMgSi_2O_6$ with w = +1,

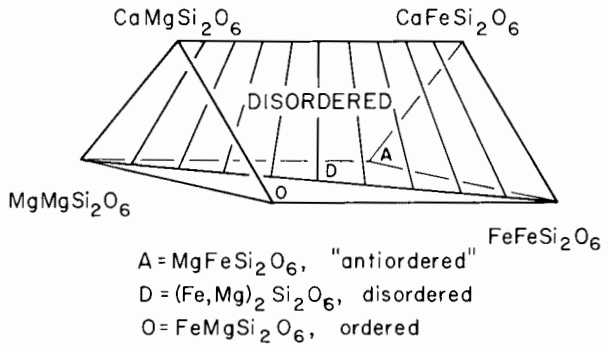

Fig. 4. Order—disorder fields in clinopyroxene.

to the hypothetical anti-ordered form, $MgFeSi_2O_6$ with w = −1, through all possible intermediate states including that of total disorder. Computed points are indicated by circles, and standard deviations by curves above and below the lines. The values of the index n_z, the extinction angle Z/c, and perhaps the birefringence n_z – "n_x" offer the best possibility for establishing a correlation between the order parameter w and a measurable quantity that might be used to evaluate it. The regression equations were derived under the assumption that w = +1 for all specimens considered. If this assumption is wrong, then residuals from removal of the regression, E in table 3, may be correlated with the order parameter w. Figure 4 shows that the greatest sensitivity for such a correlation should be associated with specimens whose compositions are close to clinohypersthene, $FeMgSi_2O_6$.

"PURE" CLINOHYPERSTHENE, $FeMgSi_2O_6$

We must compare the data of figure 5 for pure $FeMgSi_2O_6$ with data measured in specimens of the same composition. There are no such specimens, however, but only some that approach this composition. The regression con-

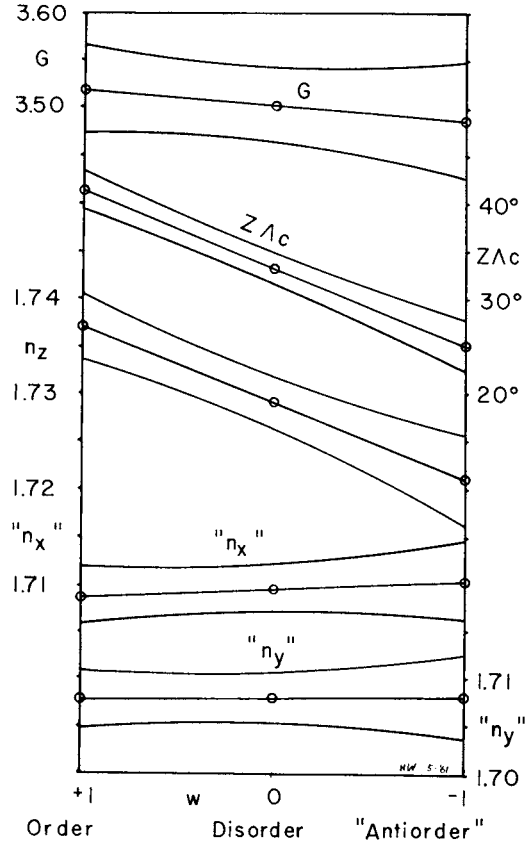

Fig. 5. Properties of clinopyroxene.

stants of table 4 properly can be used to remove the effects of "impurities" present in such specimens and thereby derive valid estimates of their properties as if they were "pure." The eight specimens that are closest to the desired composition are numbered 24, 29, 30, 33, 34, 75, 76, and 77 in table 2. Their compositions and properties are repeated in table 8 for convenience in the following discussion:

> The composition of interest here is represented by all $x_i = 0$ except $x_9 = 1.000$. For example, specimen 24 with $n_z = 1.722$ has $x_1, x_2, \ldots, x_{12}$, respectively equal to .018, .026, .000, .005, .007, .000, .000, .317, .522, .018, .013, and .000. The effect of the Al in position C is removed by subtracting from 1.722 the product of .018 ($= x_1$) and +.0387 ($= b_{13}$ from table 4); the effect of each of the other components is likewise removed by subtracting $b_{i3}x_i$, except that we must allow for the effect of *increasing* the Fe″ in A by *adding* $b_{93}(1.000 - x_9)$. Careful account must be kept of the signs of the b_{ip} in this process. The result for No. 24 is as follows: $y^*_3 = n^*_z = 1.722 - (.0387)(.018) - (.0216)(.026) - (0) - (.0815)(.005) - (.1251)(.007) - (0) - (0) + (.0341)(.317) + (.0424)(1.000 - .522) - (.0225)(.018) - (.0511)(.013) - (0) = 1.7276.$

The y^*_p resulting from such adjustments are assembled for the eight most significant specimens in table 8. We are here interested in the residual *dis*agreement of the individual cases, for we hope to find a relation between these residuals and our estimate of the order parameter w (in passing we note with satisfaction the excellent agreement between the *mean* values $\bar{y}^*_p$ and the values y'_p predicted by regression).

The legend to table 8 shows that specimens 24, 29, 30, 33, and 34 are from volcanic lava flows, and that 75, 76, and 77 are from much larger bodies, which must have cooled more slowly. The more slowly cooled specimens had more time to become ordered at lower temperatures and may be presumed to have w closer to +1; in the lava-flow specimens, w may be smaller and is likely to be variable because we do not know the sizes of the lava flows concerned.

Unfortunately, there seems to be no simple relation: the slowly cooled specimens are indeed grouped much more closely, and much nearer to the regression-predicted values, especially for n_z and Z/c; the lava-flow specimens average about the same, but their spread is several times as great, and the suspicion is that some of the flows may have been rather thick. The sample is too small to be conclusive. Better control of the volcanic specimens is needed, and the difference in variability should be studied by further examples. Possibly a total recalculation of the regressions using an additional variable $w = 1$ for specimens from large bodies, and $w = 0$ for specimens from small extrusive bodies, would develop the information desired. Information on w is lacking, or at best dubious, for many specimens, and becomes less discriminating as the composition changes away from $FeMgSi_2O_6$.

ARTIFICIAL CHANGES OF ORDER AND DISORDER

A promising alternative procedure would be to redetermine optical properties of low-temperature specimens after heating them almost to their melting

TABLE 8*

Clinopyroxene specimens with compositions close to that of clinohypersthene, $FeMgSi_2O_6$, from tables 2 and 3, part II

Components	Spec. No.	24	29	30	33	34	75	76	77	Remarks
					Composition					
Al(C)	x_1	.018	.037	.028	.033	.035	.036	.014	.055	
Fe″′(C)	x_2	.026	.067	.069	.037	.000	.000	.000	.000	
Al(B)	x_3	.000	.000	.000	.000	.008	.037	.035	.016	Should be zero for pure $FeMgSi_2O_6$
Fe″′(B)	x_4	.005	.029	.037	.076	.052	.005	.002	.021	
Ti(B)	x_5	.007	.018	.021	.019	.026	.015	.014	.005	
Fe″(B)	x_6	.000	.026	.000	.000	.163	.000	.093	.046	
Mn(B)	x_7	.000	.000	.000	.000	.000	.000	.000	.000	
Mg(A)	x_8	.317	.000	.001	.004	.000	.037	.000	.000	
Fe″(A)	x_9	.522	.553	.576	.760	.752	.744	.777	.794	Should be 1.000
Mn(A)	x_{10}	.018	.018	.025	.080	.033	.016	.019	.012	
Na(A)	x_{11}	.013	.050	.028	.000	.019	.007	.002	.000	Should be zero
K(A)	x_{12}	.000	.009	.005	.000	.005	.000	.000	.000	
					Values of properties y_p					
$y_1 =$ "n_x"		1.698	1.709	1.711	1.713	1.7137	1.6988	1.7066	1.7095	
$y_2 =$ "n_y"		1.695	1.711	1.713	1.713	1.7137	1.6980	1.7055	1.7085	Observed values (*=not stated)
$y_3 = n_z$		1.722	1.738	1.739		1.7417	1.7288	1.7325	1.7360	
$y_4 = Z/c$		42	*	*	*	39	40	42	40	
$y_5 = G$		3.51	*	3.52	3.58	3.44	*	*	*	
					Values y^*_p after correction for impurities					$\bar{y}^*_p$	y'_p (Tab. 5)
y^*_1		1.7192	1.7144	1.7170	1.7088	1.7037	1.7071	1.7086	1.7109	1.7112	1.7089
y^*_2		1.7150	1.7120	1.7152	1.7060	1.7009	1.7052	1.7065	1.7085	1.7087	1.7079
y^*_3		1.7276	1.7444	1.7465		1.7314	1.7392	1.7358	1.7384	1.7369	1.7370
y^*_4		48.9°				35.8°	41.1°	41.9°	39.9°	41.5	41.4
y^*_5		3.614		3.556	3.553	3.439				3 540	3.519

References for table 8

No. 24. Pigeonite from Hakone Volcano, lava flow. Zoned: less calcic cores and more calcic mantles; $n_z = 1.720$ to 1.725, $Z/c = 42$; $x = b$. Associated with hypersthene microphenocrysts (Kuno and Nagashima, 1952).

No. 29. Subcalcic augite from hypersthene basalt lava of Sept. 1950 from Mihara-yama crater, O-sima Island (Kuno, 1955,* no. 8).

No. 30. Subcalcic augite from hypersthene basalt of 1778 from Mihara-yama crater, O-sima Island (Kuno, 1955*).

No. 33. Ferropigeonite from ejected block of remelted quartz diorite deposited in pumice from Hakone Volcano (Kuno, 1955,* no. 15).

No. 34. Ferropigeonite from ferropigeonite andesite at Loch Scridain, Mull (Kuno, 1955,* no. 16; Hess, 1949,* no. 44).

No. 75. Pigeonite from coarse, diabasic pegmatite, Goose Creek, Virginia (Hess, 1949,* no. 41).

No. 76. Pigeonite from near center of 1750-foot-thick diabase sill, Lambertville, New Jersey (Hess, 1949*, no. 42).

No. 77. Pigeonite from Moore County, North Carolina meteorite (Hess, 1949*, no. 43).

* See references in Part II.

points and then quenching them; likewise, volcanic specimens should be treated under suitable conditions at relatively low temperature to see if their physical properties would reflect an ordering transformation. Both types should also be compared further by precise X-ray methods to establish whether or not disorder does actually exist (Morimoto, Appleman, and Evans, 1959).

COMPARISON WITH RESULTS OF GRAPHICAL METHODS

Another approach to the question of evidence for disorder of the cations is to test agreement between predictions by the regressions and predictions by means of graphical methods. Hess (1949) published some well known charts for estimating the optical properties of common clinopyroxenes. His plates I–IX were constructed on a diagram shaped like figure 1. They differ from figure 1 in not distinguishing positions A and B in the formula, in assuming variable, unspecified but "average" amounts of extraneous components such as Al, and by grouping Fe‴ and Mn with Fe″, so as to reduce the number of independent composition-variables.

Hess' charts show no change in slope in the vicinity where we expect a break, but they were presumably drawn so as to smooth any such effect and spread it over a wide area. A comparison of the residual differences, E, between observed and regression-predicted values of optical properties on the one hand, and the residual differences, E′, between the observed and Hess-chart-predicted values on the other, would seem to be promising, especially for specimens with compositions close to $FeMgSi_2O_6$. The residuals, E, have already been tabulated for regression-predicted values: 155 examples are given in table 3; the few with the most suitable compositions are reviewed in table 9, together with corresponding values, E′, the errors obtained in predicting properties with Hess' charts.

For these specimens the mean residuals, E, by regressions are closer to zero than the residuals, E′, by Hess' charts, but the root-mean-square residuals that measure variability do not look significantly different. Large differences would be surprising in any case. The differences in the means of the residuals may be too small to be significant; a systematic difference might be related to the assumptions of order in the regressions, versus the rounding of the slope-change in the charts of Hess. Again, there are too few specimens.

INTERNAL EVIDENCE IN TABLES 2, 3

An attempt to use most or all of the list of 155 specimens by classifying them into three groups, namely, (1) those described as from lava flows or volcanic ejecta, (2) those from metamorphic and larger igneous bodies, and (3) those for which such data are unknown or very doubtful, was not satisfactory. Some must be included in class (3) for lack of data; some with especially high tenor of (Na.K) probably should have been but were not; many are doubtful even though described as from well known volcanic areas, because distinction is rarely made between thick and thin sills or dikes, and even between thin lava flows and thick or ponded ones. The mean deviation E_3 (for n_z) is +.00015 for 32 specimens thought to be quenched from high temperature and +.00040 for 98 probably low-temperature ones. The root-mean-square

TABLE 9

Residuals E = n(observed) − n(calculated) for certain pigeonites

Number	Calculated by regression			Calculated by Hess' chart			Composition*		
	$E(n_x)$	$E(n_y)$	$E(n_z)$	$E'(n_x)$	$E'(n_y)$	$E'(n_z)$	Ca	Mg	Fe
24	+.0103	+.0070	+.0124	+.0125	+.0110	+.0145	8	64	28
29	+.0055	+.0040	+.0074	+.0010	+.0121	+.0150	20	46	34
30	+.0081	+.0073	+.0095	+.0120	+.0135	+.0065	19	46	35
33	−.0001	−.0019		+.0055	+.0070		7	45	48
34	−.0051	−.0070	−.0049	+.0002	+.0012	+.0007	8+	39	52+
75	−.0018	−.0027	−.0038	−.0002	−.0005	+.0043	9+	51−	40−
76	−.0003	−.0014	−.0011	+.0006	.0000	−.0005	9+	44+	46+
77	+.0019	+.0005	+.0013	+.0045	+.0050	+.0055	10	46	44
Mean	+.00231	+.00072	+.00196	+.00489	+.00616	+.00657			
Root-mean-square	.00542	.00475	.00697	.00664	.00817	.00868			

* The composition columns (data from original paper in each case) represent the coordinates for projection on a triangular diagram with Ca, Mg, and (Fe,Mn,Fe‴) at the corners, as plotted by Hess (1949) in his plates I, II, and III. The signs + and − after these coordinate numbers indicate fractional parts omitted. For key to specimen numbers, see table 8.

deviations $s(E_3)$ by groups are .0057 for the quenched volcanics, and .0060 for the slowly cooled specimens. The difference between the two means is therefore not significant.

INTERNAL EVIDENCE IN THE REGRESSION COEFFICIENTS

A comparison of the effect of substituting Fe″ for Mg in position B with the effect of the same substitution in position A is especially significant in the context of the order-disorder problem. Reference to table 11 shows that the t-test establishes "likeness" of the effects of this substitution on indices "n_x" and "n_y", and specific gravity G, but "difference" at high confidence levels for n_z and for the extinction angle Z/c. The same properties were selected on the basis of figure 5. The derivation of these details is considered in Part IV below. The inference is clear that n_z and Z/c should be capable of distinguishing between ordered and disordered specimens.

SUMMARY OF ORDER-DISORDER RELATIONS

The internal optical evidence so far developed seems essentially noncommittal, or only very slightly in favor of the existence of disordered distribution of Mg and Fe″ in a few clinopyroxenes. A test comparison of physical properties calculated by regressions based on assumed perfect order, with observed data on specimens with presumably different degrees of order, suggested a slight increase of residual variance among disordered specimens, but the number of critical examples available was insufficient to make the small difference significant.

A second test showed small differences between the residual errors of prediction by the regression formula and errors of prediction by means of generally accepted two-dimensional charts. In this case the more disordered specimens show slightly more difference in residual error of prediction than the ordered ones; again the number of examples is too small. The standard charts do not take account of a break that should be present in the slopes of curves expressing physical properties if the cation-distribution is ordered, but the comparison was not designed to verify or test the charts, and should not be so used.

The alternative hypothesis that all clinopyroxenes are essentially perfectly ordered ($w = 1$) needs to be tested further. It is the basis of the regression calculations and it causes a slight break in the slopes of contour lines in figures 2 and 3. Present data strongly support but perhaps do not prove the existence of these breaks. If disordered specimens exist (or can be prepared), we may expect that at least the index n_z and extinction angle Z/c will be useful in distinguishing them, and may perhaps permit an evaluation of the degree of disorder.

PART IV. THE EFFECTS OF PARTICULAR CATION SUBSTITUTIONS ON PHYSICAL PROPERTIES

ABSTRACT. Student's t-test can be used not only to show whether individual regression coefficients differ significantly from zero but also for comparing two such coefficients, or comparing the sum or difference of two with that of two others.

The following statements, made with high confidence, are based only upon internal statistical evidence of the data on 155 clinopyroxenes described in part II: (1) The following cation substitutions have significantly different effects on the physical properties named in parentheses:

Al for Si in C compared with Al for Mg in B (all n's)
Fe‴ for Si in C compared with Fe‴ for Mg in B (extinction angle Z/c)
Fe″ for Mg in B compared with Fe for Ca in A (all n's).

(2) The data do not permit such statements respecting the substitution of Mn for Mg, compared with that of Mn for Ca.

Furthermore, the *position* in which a *given substitution* takes place may and frequently does affect the result of the substitution significantly. Thus when Fe‴ for Al in position C is compared with the same substitution Fe‴ for Al in B, the effects on all optical properties are significantly different; likewise comparing Fe″ for Mg in B with Fe″ for Mg in A shows significant differences for the effects on n_z and on Z/c; finally *the data studied* show no statistical evidence of a significant difference between Mn for Mg in B and in A. Further study using these data should permit estimating the degree of cation disorder if such disorder exists in specimens quenched from high temperatures.

GENERAL

Notwithstanding the implications of some titles in the literature (Hori, 1954, 1956; Henriques, 1958a,b,c), it seems to be impossible to estimate the effect of inserting a particular constituent, independently of the effect of the removal of whatever it replaces; even if it fills an otherwise vacant lattice site, it is replacing a hole, and the effect of the hole must be considered. Thus we can estimate the effect of a cation substitution but not of a single cation. If the substitution is linked to another valence-balancing substitution, the situation is more complicated but quite as soluble. From this point of view, it may be more convenient to consider the problem in terms of end members, much as one would consider the properties of a vector in terms of its components parallel

to arbitrarily selected axes. The extrapolated properties of certain end members of clinopyroxene were given in table 5.

Nevertheless, it is important to compare the effects of various cation substitutions, and for this purpose Student's *t-ratio*, defined as the ratio of a quantity to its own standard error (Davies, 1958; also Hey, 1956, for an example in mineralogical context), permits comparison of a regression coefficient with zero (or other constant) to determine the level of confidence with which one can assert that the coefficient "does not differ significantly" from zero (or the constant). This test was used in Part II, table 4, to detect the regression coefficients that appear to be not significantly different from zero, at a confidence level of about 30 percent ($p = 0.30$). Such coefficients are starred in the table, and for empirical, purely descriptive purposes, the regressions might be somewhat improved if the starred coefficients were arbitrarily set equal to zero and the others adjusted correspondingly. The t-test takes into account only the internal statistical evidence of the numbers used and cannot tell us whether or not the physical situation is better met by setting such coefficients equal to zero.

Physical reasons led Henriques (1958c) to accept a large number of regression coefficients whose t-ratios were much smaller than 1.0, whereas Hey (1956) carried out the adjustments necessary to remove such coefficients. Many statisticians would probably require a t-ratio of about 2.0 (confidence level about 0.95 = 95 percent, that the quantity differs significantly from zero). The elimination procedures are well known (Davies, 1958; Hey, 1956; and many others) and easy to apply, though somewhat tedious without at least a desk-type calculator.

COMPARISON OF TWO REGRESSION COEFFICIENTS

The formula for the standard deviation $s_{i\text{-}j}$ of the difference of two regression coefficients $b_{ip} - b_{jp}$ uses the elements c_{ij} of the appropriate covariance matrix (here, p in table 6),[3] as follows:

$$s_{i\text{-}j} = s_p \left(\frac{N(c_{ii} + c_{jj} - 2c_{ij})}{N\text{–}R\text{–}1} \right)^{1/2}$$

Here N represents the number of observations, and (N–R–1) is the number of degrees of freedom.

Forming the ratio $t_{i\text{-}j} = (b_i - b_j)/s_{i\text{-}j}$, we obtain

$$t_{i\text{-}j,p} = \frac{(b_{ip} - b_{jp})}{s_p} \left(\frac{N\text{–}R\text{–}1}{N(c_{iip} + c_{jjp} - 2c_{ijp})} \right)^{1/2}$$

For example, the difference between coefficients for Al(C) and Al(B), for n_x (i.e., first equation, $p = 1$), requires the values $N = 155$, $R = 12$, $s_1 = .00571$, $b_{11} = +.0460$, $b_{31} = -.0341$ from table 4, and the values $c_{111} =$

[3] In table 6, Part II (Winchell, 1961, p. 316) column 9, headed "Fe" a", should be amended in the first matrix to read as follows: –0.062 +0.240 –0.379 +0.059 +0.110 –0.951 +0.065 +0.413 +0.054 +0.340. In the second matrix the eighth entry in column 9 should read +0.065 instead of +0.085. In the third matrix, same column, the 0.270 is positive. Equation (3) is quoted correctly on page 309; the factor 2 was omitted before the double summation on page 317.

$+5.268$, $c_{331} = +5.403$, and $c_{131} = -3.318$ (and $s_1 = .00571$) from table 6; thus

$$t_{1\text{-}3,1} = \frac{0.0801}{0.00571}\left(\frac{142}{155(5.268 + 5.403 + 6.636)}\right)^{1/2} = 3.24$$

For more than 120 degrees of freedom a t-value of 3.29 would mean a confidence level of 0.999[4] in the hypothesis that the numerator of the t-ratio is not zero, so that a t-value of 3.24 in this case is quite sufficient to warrant concluding that the substitution of Al for Si in C has an effect that is significantly different from the effect of substitution of Al for Mg in B. In this case the conclusion is obvious, anyway, from the fact that the regression coefficients concerned have opposite signs and are both significantly different from zero (see table 4). Equally high confidence levels are not possible for comparison of regression coefficients for some other pairs of substitutions, as shown in table 10.

TABLE 10

t-Values for certain $b_{ip} - b_{jp}$ in clinopyroxene

i j	Components	$t_{i\text{-}j,1}$	$t_{i\text{-}j,2}$	$t_{i\text{-}j,3}$	$t_{i\text{-}j,4}$	$t_{i\text{-}j,5}$
1 3	Al for Si in C Al for Mg in B	3.24	4.01	3.97	1.36	1.51
2 4	Fe‴ for Si in C Fe‴ for Mg in B	0.87	1.23	1.44	3.09	1.40
6 9	Fe″ for Mg in B Fe″ for Ca in A	4.29	5.83	4.23	0.60	0.36
7 10	Mn for Mg in B Mn for Ca in A	0.14	0.20	0.19	0.17	0.50
Degrees of freedom*		142	142	142	127	66

* The confidence levels for more than 60 degrees of freedom are approximately $p = 0.3$ for $t = 1.0$, 0.2 for $t = 1.3$, 0.1 for $t = 1.7$, 0.05 for $t = 2.0$, 0.02 for $t = 2.4$, 0.01 for $t = 2.7$ (Fisher and Yates, 1957).

Evidently the regression data clearly distinguish between the effects of substitution of Al in B or C, Fe‴ in B or C, Fe″ in A or B, but not Mn in A or B. The lack of discrimination in the case of Mn may be either (a) that insufficient data (or improperly distributed samples) have been studied, or (b) that Mn replacing Ca in A really has almost the same effect as Mn replacing Mg in B. Regardless of conclusion (b), table 1 shows that better data would be desirable.

EFFECT OF CRYSTALLOGRAPHIC POSITION ON REPLACEMENT EFFECTS FOR A GIVEN PAIR OF ELEMENTS

We have seen that with the exception of Mn, replacements by a single element of the standard ones for positions A, B, or C in the pyroxene formula ABC_2O_6 do generally have significantly different effects. A more sophisticated inquiry as to the comparative effects of one and the same replacement, as Fe for Mg in two structurally different positions such as A and B, may be much

[4] Strictly, the t-ratio gives evidence about the converse of this statement, i.e., that the confidence level is only 0.001 for the hypothesis that the numerator ($b_{11} - b_{31}$) is *not* significantly different from zero.

more interesting, for a difference in that case would suggest that the effect of disorder can be studied optically.

Such a study is possible because we know the effect of replacing Ca by Mg in A, and can therefore remove that part of the effect of replacing Ca by Fe in A by subtracting the appropriate regression coefficient from that for replacement of Ca by Fe. Thus the effect of substitution of Fe″ for Ca in A is given by b_{9p}; the effect of substitution of Mg for Ca in A is removed from this by subtracting b_{8p}, and the difference measures the effect of replacing Mg by Fe″. The comparison is as follows:

Substitution of Fe″ for Mg in B:		b_{6p}
Substitution of Fe″ for Ca in A:	b_{9p}	
Correction for prior substitution of Mg for Ca in A:	$-b_{8p}$	
Substitution of Fe″ for Mg in A:		$b_{9p} - b_{8p}$
Difference (= numerator of t-ratio)		$b_{6p} - b_{9p} + b_{8p}$

For the index n_z, p = 3, and the quantities for comparison are b_{63} and $(b_{93} - b_{83})$. The t-test requires the ratio of the difference of these quantities to the standard error of that difference:

$$t_{(6\text{-}9+8),3} = (b_{63} - b_{93} + b_{83})/s_{(6-9+8),3}$$

where $$s_{(6-9+8),3} = s_3 \left(\frac{N(c_{66} + c_{99} + c_{88} - 2c_{69} - 2c_{89} + 2c_{68})_3}{N-R-1} \right)^{1/2}$$

The b's, s_3, N, and (N–R–1) are given in table 4; the c's and s_3 are in table 6: substitution in the formula gives

$$t_{(6\text{-}9+8),3} = \frac{(+.0606 - .0424 - .0341)}{.00630} \left(\frac{142}{155\,(+.226 + .340 + .354 - .130 - .108 + .124)} \right)^{1/2}$$

$$= \frac{-.0159}{.00630} \left(\frac{142}{155 \times .806} \right)^{1/2}$$

$$= 2.69$$

Replacement of Mg by Fe″ therefore has a significantly different effect upon n_z *depending upon the lattice position where the replacement occurs.*

Table 11 shows the effects of particular substitutions in one position compared with that of the same substitution in another position for several substitutions. We conclude with good confidence (p = 0.95 or 95% for t = 2.00) that all optical properties (but, understandably, not G) are affected in significantly different ways depending upon the position where the substitution of Fe‴ for Al (i.e., in C or in B of ABC_2O_6) takes place, that only n_z and the extinction angle Z/c are significantly affected by the position (A or B) in which substitution of Fe″ for Mg takes place, and that neither optical properties nor G are significantly affected by the position in which Mn replaces Mg

or Fe″. The last conclusions might be different if better data on Mn were available. for the standard errors of the regression coefficients describing behavior of the physical properties with respect to Mn substitutions are much higher than those of the other coefficients; that in turn reflects upon the scarcity of fully substituted Mn-pyroxenes, and insufficient data for such pyroxenes as johannsenite and schefferite.

TABLE 11

Differences, standard deviations, and t-ratios for significance of differences, between effects of identical substitutions in distinct lattice positions

Substitutions and positions involved	Effect calculated by regression, symbolic	p = 1 Effect on n_x	2 Effect on n_y	3 Effect on n_z	4 Effect on Z/c	5 Effect on G
Fe‴ for Al in C	$b_{2p}-b_{1p}$	+.0021	−.0065	−.0171	−8.4	+.550
	s	±.0359	±.0372	±.0396	±26.3	±.450
in B	$b_{1p}-b_{3p}$	+.1151	+.1456	+.1529	+55.6	+.312
	s	±.0061	±.0064	±.0068	±7.5	±.080
Difference D	$b_{2p}-b_{1p}-b_{1p}+b_{3p}$	−.1130	−.1521	−.1700	−64.0	+.238
	s of D	±.0367	±.0381	±.0404	±28.6	±.449
t-ratio of D		3.08	3.99	4.20	2.24	0.53
Fe″ for Mg in B	b_{9p}	+.0602	+.0598	+.0606	+2.7	+.278
	s	±.0027	±.0028	±.0030	±1.8	±.041
in A	$b_{9p}-b_{8p}$	+.0586	+.0595	+.0765	+19.0	+.310
	s	±.0046	±.0048	±.0050	±3.0	±.074
Difference D	$b_{8p}-b_{9p}+b_{8p}$	+.0016	+.0003	−.0159	−16.3	−.032
	s of D	±.0054	±.0056	±.0059	±3.6	±.080
t-ratio of D		0.30	0.05	2.69	4.57	0.40
Mn for Mg in B	b_{7p}	+.0292	+.0345	+.0337	+8.6	+.257
	s	±.0124	±.0129	±.0137	±8.3	±.561
in A	$b_{10.p}-b_{8p}$	+.0520	+.690	+.0566	+19.1	+.777
	s	±.0432	±.0448	±.0476	±30.7	±.814
Difference D	$b_{7p}-b_{10.p}+b_{8p}$	−.0228	−.0345	−.0229	−10.5	−.520
	s of D	±.0526	±.0546	±.0580	±37.3	±.936
t-ratio of D		0.43	0.63	0.39	0.28	0.56
Fe″ for Mn in B	$b_{8p}-b_{7p}$	+.0310	+.0253	+.0269	−5.9	+.021
	s	±.0130	±.0135	±.0143	±8.7	±.633
Fe″ for Mn in A	$b_{9p-10.p}$	+.0066	−.0095	+.0199	−0.1	−.467
	s	±.0444	±.0462	±.0490	±31.3	±.661
Difference D	$b_{8p}-b_{7p}-b_{9p}+b_{10.p}$	+.0244	+.0348	+.0070	−5.8	+.488
	s of D	±.0532	±.0553	±.0587	±37.4	±.962
t-ratio of D		0.45	0.63	0.12	0.16	0.51
Degrees of freedom		142	142	142	127	66

SUMMARY

Single elements that can substitute independently for two different components (as for Ca and Mg, or for Mg and Si) of diopside, $CaMgSi_2O_6$, have significantly different effects on the physical properties in the two different positions. Data on Mn replacing Ca, and Mn replacing Mg are too meager to establish significance of the difference for these cases.

In cases where the *same* two elements participate in exchanges at two different lattice sites, certain physical properties may be distinct; if so, the properties concerned may serve in very important studies of possible cation disorder.

PART V. ALTERNATIVE FUNCTIONS OF REFRACTIVE INDEX

ABSTRACT. The positive and negative first and second powers of refractive index n_b are predicted with equal precision by regression equations, showing that there is no empirical advantage in substituting dielectric constants or dielectric impermeabilities for refractive indices in regressions of these properties on crystal-chemical composition-parameters in clinopyroxene.

GENERAL STATEMENT

Linear regressions of refractive indices on composition-parameters are attractive, convenient, but purely descriptive tools unless there is some physical reason to suppose that such linear relations are justified. Some objections and reservations lead to easily tested hypotheses: first, the refractive indices and extinction angles constitute an inhomogeneous set of data describing the dimensions and orientation of the optical indicatrix. One homogeneous set would be the six indices of refraction for light vibrating parallel to the axes c, b, $\perp$ (100) and the bisectors of the three plane angles between pairs of these directions. Calculations of the refractive indices for these directions would be tedious, but the resulting set of index-data would be homogeneous and might therefore be preferable. One of these directions is the symmetry axis b, so that the only calculations really required would be for vibrations parallel, perpendicular, and at 45° to c in (010). The data already presented in Part II do not indicate a significantly better regression for y_2 (which is one of the preferred coordinates) than for y_1 and y_3 (which are minimum and maximum indices in variable directions in (010)), so it would seem unnecessary to test this hypothesis further. It is nevertheless attractive because n_z and Z/c are especially sensitive to possible variations in the ordering of Mg and Fe (see Part IV).

ALTERNATIVE FUNCTIONS

The principal dielectric constants K_i of a crystal (Nye, 1957, p. 236) are related to the principal refractive indices by three equations:

$$K_i = n_i^2 \qquad (i = X, Y, Z)$$

The dielectric constants form a second-rank tensor, and might be a preferable set of dependent variables for the regressions.

The relative dielectric impermeabilities $B_i = 1/K_i = 1/n_i^2$ (Nye, 1957, p. 237) also transform as a second-rank tensor and might therefore be preferable to the refractive indices. For purposes of a test, it seems unnecessary to

calculate the regressions of all four of the independent constants of each of these tensors. Data for one fixed axis (b) are already at hand, and were therefore used for test.

New regressions of $y_6 = (n_b)^2$, $y_7 = (n_b)^{-1}$, and $y_8 = (n_b)^{-2}$ were computed, using the 155 clinopyroxenes described in Part II. The resulting regression constants, matrices of moments and of covariances, and other summary data were obtained for comparison with the results reported in Part II. Because these regressions do not give better results than the direct regressions of principal refractive indices on the same composition data, they are not quoted in full here.[5] The standard error of regression s_p, for example, was 0.00593 for $p = 2$ (regression of n_b on composition); those for the three new regressions, $p = 6$, 7, and 8, are .020437, .002002, and .002337, respectively, which, on being converted to units comparable to the units of s_2 and n_b, become $s_p' = .0060$, .0058, and .0058. Similarly the multiple coefficients of determination, R_p^2, for regressions $p = 2$, 6, 7, and 8, are all nearly equal: .965, .966, .965, and .964, respectively; finally, the corresponding F-ratios are 330.4, 332.3, 325.0, and 320.2.

APPLICATION TO COMPOSITIONS WITH LARGE RESIDUALS

An additional test to determine whether any of these regressions might possibly be better than the original one ($p = 2$) for the less well represented compositions was made by studying data on the 24 specimens with largest residuals E_2, E_6, E_7, and E_8. We assume that, although a few badly aberrant specimens containing major errors may be included, such a list is long enough to include mostly valid observations. The agreement between the refractive index values derived from these four regrssions ($p = 2$, 6, 7, and 8) is considerably better than that between the observed and the calculated values! This is in clear agreement with the similarity of the summary statistics. The total range of variation of refractive index n is evidently too small for the curvatures corresponding to substitutions of the positive and negative first and second powers of n to become significant. Thus for purposes of empirical prediction of n_b, any of the regressions $p = 2$, 6, 7, or 8, is as good as any other.

CONCLUSION

Regression of the refractive index n_b on the composition of clinopyroxene is empirically as good as regressions of its reciprocal, its square, and the reciprocal of its square, and is more convenient.

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[5] Copies of the matrices of moments and of covariances, together with complete lists of regression constants with standard errors and t-ratios, and lists of the actual input data and residuals, have been deposited as Document No. 7365 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document Number and remitting $6.25 for photoprints, or $2.50 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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References

Davies, O. L., ed., 1958, Statistical methods in research and production, 3rd ed.: London, Oliver and Boyd, and New York, Hafner, 396 p.

Fisher, R. A., and Yates, Frank, 1957, Statistical tables for biological, agricultural, and medical research: New York, Hafner, 140 p.

Ghose, S., 1960, Mg-Fe ordering in some ferromagnesian minerals: Am. Crystallog. Assoc. Program and Abs., Washington, Jan. 24-27.

Henriques, A., 1958a, An attempt to determine the effect of cations on the extinction angle c/Z with the aid of linear regression equations: Arkiv Mineralogi Geologi, v. 2, p. 337-340.

———— 1958b, The influence of cations on the optical properties of clinopyroxenes, Part I: Arkiv Mineralogi Geologi, v. 2, p. 341-348 [Linear regressions for refractive indices and 2V].

———— 1958c, The influence of cations on the optical properties of clinopyroxenes, Part II: Arkiv Mineralogi Geologi, v. 2, p. 381-389. [Regressions with second-degree terms].

Hess, H. H., 1949, Chemical composition and optical properties of common clinopyroxenes, Part I: Am. Mineralogist, v. 34, p. 621-666.

———— 1952, Orthopyroxenes of the Bushveld type, ion substitutions and changes in unit cell dimensions: Am. Jour. Sci., v. 250A (Bowen vol.), p. 173-187.

Hey, M. H., 1956, On the correlation of physical properties with chemical composition in multivariate systems: Mineralog. Mag., v. 31, p. 69-95.

Hori, Fukutaro, 1954, Effects of constituent cations on the optical properties of clinopyroxenes: Tokyo Univ., Coll. Gen. Education, Sci. Papers, v. 4, p. 71-83.

———— 1956, Effects of constituent cations on the refractive indices of orthopyroxenes: Mineralog. Jour. [Japan], v. 1, p. 359-371.

Kuno, Hisashi, 1955, Ion substitution in the diopside-ferropigeonite series of clinopyroxenes: Am. Mineralogist, v. 40, p. 70-93.

Kuno, Hisashi, and Hess, H. H., 1953, Unit cell dimensions of clinoenstatite and pigeonite in relation to other common clinopyroxenes: Am. Jour. Sci., v. 251, p. 741-752.

Kuno, Hisashi, and Nagashima, Kōzō, 1952, Chemical compositions of hypersthene and pigeonite in equilibrium in magma: Am. Mineralogist, v. 37, p. 1000-1006.

Morimoto, N., Appleman, D. E., and Evans, H. T., Jr., 1959, Structural relations between diopside, clinoenstatite, and pigeonite: Carnegie Inst. Washington, Ann. Rept. Director Geophys. Lab. for 1958-59, p. 193-197.

———— 1960, The crystal structures of clinoenstatite and pigeonite: Zeitschr. Kristallographie, v. 114, p. 120-147.

Nye, J. F., 1957, Physical properties of crystals: Oxford, Clarendon Press, 322 p.

Winchell, Horace, 1961, Regressions of physical properties on the compositions of clinopyroxenes. II. Optical properties and specific gravity: Am. Jour. Sci., v. 259, p. 295-319.

Winchell, Horace, and Tilling, R. I., 1960, Regressions of physical properties on the compositions of clinopyroxenes. I. Lattice constants: Am. Jour. Sci., v. 258, p. 529-547.