UNIT CELL DIMENSIONS AND IONIC SUBSTITUTIONS IN COMMON CLINOPYROXENES

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Abstract

The unit cell dimensions of eight analysed-clinopyroxenes are presented. In the light of the recent researches on the cummingtonites and orthopyroxenes, the discrepancy in the clinopyroxene correlation diagram, suggested by Brown (1960), is pointed out. Though linear regression equations are found to hold good for the optical properties and the specific gravity of clinopyroxenes (Winchell, 1961), they fail to give a satisfactory correlation between the lattice constants and the chemical composition. This is found to be due to the fact that the increases in the lattice constants, especially a and β (consequently $a \sin \beta$), caused by $Mg^{2+} - Fe^{2+}$ substitution, seem to be influenced by the amount of calcium present. On the basis of these observations, a modification of Brown's correlation diagram is suggested.

Kuno and Hess (1953), Kuno (1955), Brown (1960) and Winchell (1960) have made an attempt to correlate the cell dimensions and compositions in clinopyroxenes. Details of previous work in this field have been given by Brown and Winchell. Brown showed that the two dimensions $a \sin \beta$ and b exhibit a linear variation with the substitution of Mg^{2+} by Fe^{2+}, of Mg^{2+} by Ca^{2+} and of Fe^{2+} by Ca^{2+} respectively. Winchell (1960) calculated the regression coefficients of the lattice constants on the composition of clinopyroxenes. The author (1963) observed that the relationship between $a \sin \beta$ and the composition is not strictly linear within the calcium-rich clinopyroxenes.

While working on the problem "Optical, chemical and x-ray studies of the mineral suites of some South Indian rocks," the author determined the compositions and cell dimensions of eight clinopyroxenes (Specimens A to H, Tables 1, 2). The cell dimensions of these specimens were determined by the method described elsewhere (Viswanathan, 1964) and the errors in their determination are expected to lie within ± 0.010 Å and that in $\beta \pm 10'$. All these pyroxenes were analysed carefully twice and it was observed that the discrepancy between the two values (especially for the major constituents like SiO_2, FeO, MgO and CaO) was never greater than 3% of the first value. The means of these two values were taken as final values for all the constituents. The analyses are given in Table 1 recast as atoms per 6000 oxygen. All these specimens were examined under microscope and were found to be free from exsolution.

Besides these eight specimens, the cell dimensions and compositions of twenty six more pyroxenes, taken from literature, are presented in this paper. Of these thirty four, twenty five specimens (Table 1) are free from exsolution (in twelve of them, this was determined microscopically; in

others it was assumed to be so, because they are from metamorphic or volcanic rocks). The other nine pyroxenes (Table 3) show exsolved lamellae. As the cell dimensions determined in these cases are those of the hosts, the chemical compositions of these specimens have to be corrected

TABLE 1. ANALYSES OF CLINOPYROXENES, ABC_2O_6, RECAST AS ATOMS PER 6000 OXYGEN, SHOWING ASSIGNMENT TO FORMULA POSITIONS A, B, C AND SYMBOL X_i USED IN COMPUTATION

Symbol X_i Sp. No.	Si	Al	Fe^{3+}	Al	Fe^{3+}	Ti	Mg	Fe^{2+}	Mn	Mg	Fe^{2+}	Mn	Ca	Na	K	Sum
	X_1 (Position C)			X_2			X_3 (Position B)			X_4 (Position A)		X_5				
A	1874	126	—	55	35	4	807	99	—	—	118	—	798	75	18	4009
B	1822	178	—	65	22	4	816	93	—	—	133	7	778	84	22	4024
C	1820	175	5	—	18	2	591	389	—	—	9	7	987	23	—	4026
D	1918	82	—	8	—	4	687	294	—	—	—	—	993	18	—	4004
E	1921	79	—	16	50	5	652	277	—	—	24	—	946	23	—	3993
F	1907	93	—	17	37	7	585	354	—	—	62	—	878	64	—	4004
G	1866	134	—	31	45	9	823	92	—	—	142	9	831	22	4	4008
H	1917	83	—	2	22	11	812	153	—	—	157	9	809	31	9	4015
1	1963	37	—	21	13	—	740	215	9	—	—	—	994	18	—	4010
2	1933	18	41	—	—	11	675	286	28	—	811	—	195	—	—	3998
3	2000	—	—	—	—	—	—	1000	—	—	1000	—	—	—	—	4000
4	1902	98	—	49	41*	13	897	—	—	31	113	4	830	26	1	4005
5	1882	118	—	21	55*	27	897	—	—	18	139	4	809	46	2	4018
6	1941	51	8	—	36	21	211	740	—	—	139	19	816	17	2	4001
7	1928	72	—	34	52	2	37	875	—	—	124	22	832	25	2	4005
8	1988	12	—	3	47	2	64	788	96	—	—	35	938	12	—	3985
9	1930	33	37	—	76	19	905	—	—	4	760	80	132	—	—	3976
10	1903	28	69	—	37	21	942	—	—	1	576	25	392	28	5	4027
11	1911	89	—	5	27	22	917	29	—	—	179	7	794	22	9	4011
12	1906	94	—	19	18	7	956	—	—	23	425	14	574	—	—	4036
13	1956	18	26	—	5	7	988	—	—	317	522	18	160	13	—	4030
14	1990	10	—	40	14	2	334	610	—	—	—	6	961	14	—	3981
15	1986	14	—	3	11	1	932	53	—	—	19	5	971	4	2	4001
16	2000	—	—	—	—	—	1000	—	—	1000	—	—	—	—	—	4000
17	1851	149	—	65	22	11	827	75	—	—	108	—	903	13	—	4024

* Includes Cr.

References to the analyses: A to H, (Viswanathan, 1963, nos. 1 to 7 and 9); 1, (Weibel and Locher, 1964, diopside); 2, (Morimoto et. al 1960, pigeonite); 3, (Burnham, 1965); 4, (Brown, 1956, diopside); 5, 6 and 7, (Brown, 1960, nos. 1, 10 and 11 in Table 2); 8, (Hess 1949, no. 18; Kuno and Hess, 1953, no. 6); 9, (Kuno, 1955, no. 15); 10, (Kuno, 1955, no. 9); 11, (Kuno, 1955, no. 5); 12, (Kuno, 1955, no. 6); 13, (Kuno and Nagashima, 1952, no. 3; Kuno and Hess, 1953, no. 2); 14, (Hess 1949, no. 16; Kuno and Hess, 1953, no. 5); 15, (Hess 1949, no. 35; Kuno and Hess, 1953, no. 4); 16, (Kuno and Hess, 1953, no. 1); 17, (Kuno, 1955, no. 1).

to get the accurate composition of the host (Brown, 1960). To make this correction, the exact composition of the exsolved lamellae (including those of the minor constituents like Al_2O_3, Fe_2O_3 . . . etc.) and the exact proportion of the lamellae to the host have to be determined. As this is almost an impossibility, especially when the lamellae are very thin and as the exact information concerning these details are lacking, the available

TABLE 2. CELL DIMENSIONS AND OPTICAL PROPERTIES OF CLINOPYROXENES,
WHOSE COMPOSITIONS ARE GIVEN IN TABLE 1

Sp. No.	a Å	b Å	c Å	β	$a \sin \beta$	α	β	γ	$2v$ Z	Z∧c
A	9.725	8.918	5.245	74°04′	9.354	1.683	1.690	1.711	57°	40°
B	9.723	8.913	5.241	74°05	9.350	1.683	1.689	1.709	56	39
C	9.772	8.941	5.255	74°24	9.412	1.698	1.705	1.723	62	46
D	9.749	8.937	5.228	74°36	9.398	1.692	1.699	1.718	61	42
E	9.752	8.940	5.239	74°36	9.401	1.694	1.701	1.720	60	43
F	9.761	8.949	5.250	74°22	9.401	1.696	1.703	1.724	54	43
G	9.745	8.925	5.251	73°59	9.366	—	—	—	57	42
H	9.734	8.929	5.260	74°07	9.362	1.687	1.694	1.715	58	40
1	9.763	8.951	5.251	74°30	9.408	—	—	—	59	41
2	9.731	8.953	5.256	71°27	9.225	—	—	—	—	—
3	9.720	9.098	5.234	71°34	9.221	—	—	—	—	—
4	9.734	8.907	5.246	73°51	9.350	1.682	1.687	1.709	51	—
5	9.746	8.910	5.268	73°53	9.363	—	1.691	—	47	—
6	(9.802)	9.004	(5.252)	(74°45)	9.457	—	—	—	—	—
7	—	9.024	—	—	9.486	—	—	—	—	—
8	9.854	9.024	5.263	75°40	9.548	1.723	1.730	1.751	63	48
9	9.712	8.959	5.251	71°27	9.208	1.713	1.713	(1.734)	11	—
10	9.716	8.944	5.242	72°20	9.258	1.711	1.713	1.713	25	—
11	9.744	8.909	5.260	73°28	9.341	1.690	1.696	1.716	51	5
12	9.722	8.925	5.242	72°57	9.295	1.691	1.697	1.718	44	10
13	9.692	8.917	5.239	71°27	9.185	1.695	1.698	1.722	14°*	42
14	9.804	8.980	5.259	74°46	9.460	1.708	1.714	1.736	60	43
15	9.750	8.930	5.249	74°10	9.380	1.672	1.679	1.701	57	40
16	9.618	8.828	5.186	71°38½	9.128	1.651	1.652	1.661	35°*	22
17	9.742	8.901	5.268	73°55	9.361	1.690	1.696	1.715	59	3

Values in parentheses are of doubtful accuracy (Brown, 1960) and hence they were not used for the calculation of regression coefficients.

Errors in the refractive indices, 2v and Extinction angles of specimens A to H are ±0.005, ±2° and ±2° respectively.

* X=b for Nos. 13 and 16 only; others have Y=b.

TABLE 3. UNIT CELL DIMENSIONS AND MAJOR CATION CONTENTS OF THE
CLINOPYROXENES, THE COMPOSITIONS OF WHICH HAVE BEEN
CORRECTED FOR EXSOLUTION

Specimen No.	Ca^{2+}	Mg^{2+}	Fe^{2+}	Al^{iv}	Al^{vi}	a Å	b Å	c Å	β	$a \sin \beta$ Å	Reference
1	44.3	43.2	12.5	0.099	0.032	9.751	8.926	5.260	73°57′	9.371	Brown, 1960, No. 2, Table 2
2	44.6	40.3	15.1	0.096	0.015	9.753	8.928	5.259	73°56	9.373	Brown, 1960, No. 3, Table 2
3	42.3	38.7	19.0	0.084	0.018	9.754	8.940	5.270	73°59	9.375	Brown, 1960, No. 4, Table 2
4	41.6	37.0	21.4	0.077	0.011	9.751	8.945	5.267	74°02	9.376	Brown, 1960, No. 5, Table 2
5	40.5	36.5	23.0	0.086	0.019	9.753	8.944	5.267	74°03	9.378	Brown, 1960, No. 6, Table 2
6	40.9	34.5	24.6	0.091	0.010	9.757	8.948	5.251	74°06	9.383	Brown, 1960, No. 7, Table 2
7	41.0	31.4	27.6	0.058	—	9.758	8.954	5.255	74°07	9.385	Brown, 1960, No. 8, Table 2
8	40.2	27.6	32.2	0.063	—	9.763	8.965	5.272	74°13	9.395	Brown, 1960, No. 9, Table 2
9	47.8	26.0	26.2	0.049	0.016	9.771	8.966	5.249	74°36	9.420	Binns, 1962, clinopyr. No 5

Al^{iv} and Al^{vi} denote the amount of aluminum in the tetrahedral and octahedral positions respectively.

compositions of these specimens are not considered adequately accurate for inclusion along with the other twenty five specimens for the purposes of calculating the regression coefficients. They are only plotted in the final correlation diagram presented (Fig. 3). The pyroxene (No. 1, Table 1) is from a contact rock from Bergell Valley, Switzerland (Weibel and Locher, 1964). It was found to be free from exsolution (Weibel, pers. comm.). The pyroxene (No. 9, Table 3) is from a two-pyroxene granulite from Broken Hill, New South Wales (Binns, 1962) and was found to contain exsolution lamellae of clinohypersthene containing 69 mol. per cent of the clinoferrosilite molecule (Binns and Long, 1963). The analysis of this pyroxene, which was not corrected for exsolution, is given elsewhere (clinopyroxene No. 5, Binns, 1962). A rough estimate of the abundance of (001) clinohypersthene lamellae, based on electron probe traverse is approximately 10% (Binns, pers. comm.). On this basis, the original analysis was corrected by the author, and the corrected composition is given in Table 3 in terms of Ca^{2+}, Mg^{2+} and Fe^{2+} atomic per cent. The cell dimensions of these two pyroxenes were determined by the author, following the procedure described by Viswanathan and Ghose (1965). The probable errors in the cell dimensions of these specimens are expected to lie within ± 0.005 Å and the error in $\beta \pm 5'$.

The following values were obtained for the $a \sin \beta$ and b dimensions of clinoenstatite and clinoferrosilite from Fig. 5 of Brown (1960).

	$a \sin \beta$	b
clinoferrosilite	9.330 Å	9.098 Å
clinoenstatite	−9.030 Å	−8.840 Å
	0.300 Å	0.258 Å

The total increase in $a \sin \beta$ in the clinoenstatite-clinoferrosilite series, according to Brown, is 0.300 Å, whereas the total increase in b dimension is 0.258 Å. This means that the $Mg^{2+} - Fe^{2+}$ substitution causes a greater increase in $a \sin \beta$ direction and less in b direction. It is interesting to compare this result with the orthopyroxene series and cummingtonite series. All these three series are essentially groups of minerals formed by $Mg^{2+} - Fe^{2+}$ substitution. As reported earlier (Viswanathan and Ghose, 1965), there is a remarkable similarity in the anisotropic expansions of the cell dimensions of the orthopyroxenes and cummingtonites, caused by the substitution of Mg^{2+} by Fe^{2+}. It was noted that the substitutional coefficients of expansion[1] α for the corresponding cell dimensions in both

[1] In the original paper (Viswanathan and Ghose, 1965) the actual increase in the cell dimensions has been referred to, by mistake, as the "coefficient of expansion." In a correction to this paper (to be published), the term "substitutional coefficient of expansion" has been correctly defined.

minerals are approximately the same: *e.g.* α in *a* direction of cummingtonite is 0.000135, α in *a* direction of orthopyroxene is 0.000113 and α in *b* direction of cummingtonite is 0.000288, α in *b* direction of orthopyroxene is 0.000290. The rates of expansion in *b* direction in both groups of minerals are almost double those in *a* direction (or *a* sin β direction of cummingtonite). This similarity is very interesting when one considers the differences in the structures and systems of crystallisation of these two groups. It probably means that the rate of expansion is influenced more by the nature and size of the substituting ions than by the system of crystallisation. When the values of *a* sin β and *b* of clinoenstatite and clinoferrosilite, as given by Brown's Fig. 5, are considered, it is found that the $Mg^{2+} - Fe^{2+}$ substitution causes a greater change in *a* sin β direction than in *b*. This result of Brown is incompatible with the abovementioned observations and hence it is felt that Brown's correlation diagram needs revision. But if the *b* values of Brown are used and if the coefficient of expansion ($9.098 - 8.840/100 \times 8.840$) is calculated, a value of 0.000292 is obtained, which agrees very well with the values 0.000290 and 0.000288 of orthopyroxenes and cummingtonites respectively. Therefore the discrepancy lies only in the values of *a* sin β and not in the *b* values, assigned to clinoenstatite and clinoferrosilite. This discrepancy is noted when the three pyroxenes (Nos'C', '2' and '17' Tables 1, 2) are plotted in Brown's Fig. 5. All these show *a* sin β values about 0.025 Å higher than the experimentally determined values.

Recently Burnham (1965) determined the cell dimensions of synthetic clinoferrosilite (No. 3, Tables 1, 2). Using these data and the data of synthetic cinoenstatite (No. 16, Tables 1, 2), the coefficients of expansion for the corresponding cell dimensions of these synthetic clinopyroxenes can be calculated

	a sin β Å	*b* Å
clinoferrosilite	9.221	9.098
clinoenstatite	9.128	8.828
	0.093	0.270

coefficient of expansion in *a* sin β direction $= 0.093/100 \times 9.128 = 0.000102$ coefficient of expansion in *b* direction $= 0.270/100 \times 8.828 = 0.000306$. It should be noted that these values agree very well with those of naturally occurring orthopyroxenes and cummingtonites. The coefficients of expansion for the corresponding cell dimensions in the natural clinoenstatite-clinoferrosilite series may not, therefore, differ much from that of synthetic pyroxenes. It is most likely that they are equal. Therefore, for all practical purposes, it can be assumed that the natural clinoenstatite and clinoferrosilite have the same cell dimensions as the synthetic ones

and that they show the same amount of expansion in their cell dimensions
for $Mg^{2+} - Fe^{2+}$ substitution. Further both these minerals as well as the
pigeonites, whose compositions approach the intermediate members of
the clinoenstatite-clinoferrosilite series, possess the same structure (space
group $P2_1/c$). Considering this fact and their similarity to the orthopy-
roxenes and cummingtonites, a linear increase in their cell dimensions
due to $Mg^{2+} - Fe^{2+}$ substitution can be safely assumed. Using the values
of the synthetic clinoenstatite and ferrosilite and considering a linear

FIG. 1. The plotted points refer to the clinopyroxenes for which the analyses are
given in Table 1 and the cell dimensions are given in Table 2.

relationship, the $a \sin \beta$ and b values for the clinohypersthene of the
composition $Mg_{50}Fe_{50}$ can be calculated.

$$a \sin \beta = (9.128 + 0.047) = 9.175 \text{ Å}$$
$$b \quad\ = (8.828 + 0.135) = 8.963 \text{ Å}$$

The remarkable agreement of these values with those arrived at by
Brown ($a \sin \beta = 9.18$ Å, $b = 8.97$ Å) adds much weight for accepting these
assumptions. Hence the above-referred $a \sin \beta$ values have been assigned
to clinoenstatite, clinoferrosilite and clinohypersthene ($Mg_{50}Fe_{50}$) in
Fig. 1.

In this figure the compositions of the 25 pyroxenes, given in Table 1,
have been plotted in terms of Mg^{2+}, Fe^{2+} and Ca^{2+} atomic per cent. Only
the $a \sin \beta$ values have been marked with a view to avoid confusion.
Considering the $a \sin \beta$ values of the two pyroxenes (Nos. 4 and 15,
Tables 1, 2), which lie near the diopside corner, a value of 9.375 Å has
been assigned to diopside ($Ca_{50}Mg_{50}$) arbitrarily. Similarly considering
the $a \sin \beta$ values of pyroxenes (Nos. 6, 7 and 8, Tables 1, 2), an approx-

imate value of 9.530 Å has been assigned to hedenbergite corner. From this diagram, it is seen that a change of composition from $Ca_{50}Mg_{50}$ to $Ca_{50}Fe_{50}$ causes an expansion in $a \sin \beta$, which is approximately 0.155 Å, whereas a change from $Mg_{50}Fe_{50}$ to Fe_{100} causes an expansion of only $9.220 - 9.175 = 0.045$ Å. In other words, the increase in $a \sin \beta$ caused by $Mg^{2+} - Fe^{2+}$ substitution, when $Ca^{2+} = 50$, is at least three times greater than that when $Ca^{2+} = 0$. Therefore the source of the discrepancy in Brown's diagram lies in his assumption that, for all values of Ca^{2+} content, $Mg^{2+} - Fe^{2+}$ substitution causes the same amount of increase in $a \sin \beta$.

It is seen in Table 1, that none of these twenty five pyroxenes contain large amounts of any constituent other than Si, Ca, Mg and Fe^{2+}. It may be further emphasised that this three-fold increase in $a \sin \beta$ cannot be attributed to the presence of some minor constituents. It must be attributed only to the influence of increasing calcium content and the accompanying changes in the structure. A consideration of the structure (Viswanathan and Ghose, 1965) also supports this observation. Ca^{2+} has a two-fold effect on $a \sin \beta$: (1) Because of its greater ionic size, it causes an expansion in the $a \sin \beta$ direction (2) Because it invariably occupies the M_2 site, it causes a decrease in β (obtuse angle), thereby increasing the $a \sin \beta$ value (Whittaker, 1960). To quote Brown (p. 24, 1960), "In the $a \sin \beta$ graphs, the effect (of calcium) is more marked and when changes in this dimension with $Mg^{2+}:Fe^{2+}$ substitution were graphed, the series had to be divided into a 'high-calcium' (50%) and a 'low-calcium' (40%) group."

Again, by considering the a and β values of the four pyroxenes (Nos. 4, 15, 8 and 14, Tables 1, 2) and by similar reasoning, it can be shown that the lattice constants a and β increase more rapidly, when $Ca^{2+} = 50$, than when $Ca^{2+} = 0$. But it is apparent that the amount of increase in a is smaller than that in $a \sin \beta$. The expansion in b appears to be approximately of the same magnitude, both when $Ca^{2+} = 50$ and $Ca^{2+} = 0$. The expansion in c due to $Mg^{2+} - Fe^{2+}$ substitution is too little and irregular to be commented upon.

An attempt was made to calculate the regression coefficients of lattice constants on the compositions of clinopyroxenes. Only the twenty five pyroxenes given in Table 1 were considered for this purpose. Following Winchell (1960), the analyses are recast in the form of numbers of metal atoms relative to 6000 oxygen atoms. These relative numbers of atoms are distributed according to the order of increasing ionic radius in the positions C, B and A of the pyroxene formula ABC_2O_6, thus assuming a completely ordered distribution of the elements in these positions, even though that is known to be partially untrue for pyroxenes crystallized at

high temperatures. The reader is referred to Winchell (1960) for further
details regarding the symbols and the reasons for choosing the following
five independent variables for the regression equation. The five variables
are:

$X_1 =$ Si in C position;
$X_2 =$ Al^{3+}+Fe^{3+}+Ti in B position;
$X_3 =$ Mg in B position;
$X_4 =$ Fe^{2+} in A position;
$X_5 =$ Ca in A position;

Table 4 gives the regression coefficients, Table 5 gives the lattice con-
stants of interesting compositions of clinopyroxenes, calculated using the
regression coefficients and Table 6 gives the differences between observed
and estimated values of the cell constants for the relevant analyses.
Table 6 shows satisfactory residuals for b dimension (excepting specimen
No. 2, Table 6, for which the author has no explanation at present),
thereby indicating that the regression coefficients for b are correct. But
it shows a few large residuals for $a \sin \beta$, a and β, which means that these
coefficients are incorrect. This is the root cause for the following major
discrepancies, observed in Table 5.

1) The $a \sin \beta$ value of clinoferrosilite is very high ($9.263 - 9.221 = 0.042$ Å), and that of
clinohypersthene (Mg$_{50}$Fe$_{50}$) is very low ($9.175 - 9.134 = 0.041$ Å). The $a \sin \beta$ value of
hedenbergite also appears to be low.

2) The β value of clinohypersthene appears to be low on the basis of the following con-
siderations. Clinoenstatite has a β value 71.65° and clinoferrosilite has a β value 71.57°. As
stated earlier, there are valid reasons to believe that there is a linear variation of cell
dimensions in this series. Hence, the β value for the intermediate member, clinohypersthene,
cannot be lower than 71.57° and 71.65°.

3) The a value of clinoferrosilite is very high ($9.754 - 9.720 = 0.034$ Å) and that of
hedenbergite appears to be low.

The results of Winchell's (1960) calculations also show similar dis-
crepancies between the calculated and observed a and β values of clino-
ferrosilite. It was thought that these discrepancies can be eliminated, if
the regression coefficients are calculated on 15 variables of chemical com-
position with diopside (Ca$_{50}$Mg$_{50}$) as the origin, as done by Winchell
(1961) for optical properties. As there were 12 independent variables in
the regression equation in this case, there was some general improvement,
noted in the calculated values of $a \sin \beta$ of some specimens, in s_p and R^2.
However, once again the regression coefficients for $a \sin \beta$ and β were not
satisfactory. In fact the calculated $a \sin \beta$ value of clinohypersthene
(Mg$_{50}$Fe$_{50}$) was found to be unbelievably low (9.107 Å), which is much
lower than even that of clinoenstatite. The complete results of this
calculation are not given here, as it means an unnecessary addition of
three more tables.

TABLE 4. REGRESSION COEFFICIENTS FOR CLINOPYROXENES; REGRESSION EQUATION
$$y_p = \Sigma a_{ip} X_i + s_p$$

i		0	1	2	3	4	5			
X_i		constant	$(Si)_c$	(Al $+Fe^{3+}$ $+Ti$ $)_b$	$(Mg)_b$	$(Fe^{2+})_a$	$(Ca)_a$	(5 variables, 17 degrees of freedom)		
$\bar{X}$		1.000	1.921	0.054	0.684	0.233	0.693			
p	y_p	$\bar{y}$			b_{ip} s_{ip}				s_p	R^2	F-ratio
1	a	9.740	9.375	$+.157$ .088	$+.128$ .122	$-.067$ .015	$+.066$ .021	$+.132$ .020	.0162	.885	26.38
2	c	5.247	5.138	$+.025*$ .058	$+.116$ .080	$-.0001*$ .010	$+.055$ .014	$+.061$ .013	.0107	.690	7.60
3	β	73.53	71.33	$+.757*$ 1.115	$+3.407$ 1.535	-1.182 .193	-1.146 .263	$+2.526$ .257	.204	.979	163.68
4	b	8.945	8.608	$+.171$ .052	$-.015*$ .069	$-.120$ .007	$+.134$ .012	$+.085$ .012	.0095	.973	137.74**
5	$a \sin \beta$	9.349	8.911	$+.175$ .101	$+.334$ .134	$-.128$ .014	$+.002*$ .023	$+.248$ .023	.0185	.972	134.15**

* In all these cases it may be noted that s_{ip} is greater than b_{ip}, thereby indicating that these coefficients may not be significantly different from zero.

** For these two dimensions, 5 variables; 19 degrees of freedom; 25 observations (The two additional specimens are Nos. 6 and 7 in Tables 1 and 2).

TABLE 5. ESTIMATED VALUES OF CELL DIMENSIONS FOR INTERESTING COMPOSITIONS NOT AVAILABLE IN NATURAL MATERIALS WITH THEIR RESPECTIVE STANDARD ERRORS

	Composition					Cell dimensions calculated by regression (using Table 4)				
Name	$(Si)_C$ $=X_1$	$(Al,Fe^{3+},$ $Ti)_B$ $=X_2$	$(Mg)_B$ $=X_3$	$(Mn,Fe^{2+})_A$ $=X_4$	$(Ca)_A$ $=X_5$	a Å $s(a)$	b Å $s(b)$	c Å $s(c)$	β $s(\beta)$	$a \sin \beta$ Å $s(a \sin \beta)$
Diopside	2	0	1	0	1	9.754 0.0143	8.916 0.0078	5.249 0.0094	74.19 0.180	9.380 0.0153
Hedenbergite	2	0	0	0	1	9.821 (?) 0.0118	9.036 0.0066	5.249 0.0078	75.37 (?) 0.149	9.508 (?) 0.0129
Clinoenstatite	2	0	1	0	0	9.622 0.0101	8.831 0.0059	5.188 0.0067	71.66 0.128	9.132 0.0114
Clinohy- persthene	2	0	1	1	0	9.688 0.0216	8.965 0.0124	5.243 0.0142	70.51 (?) 0.272	9.134 (?) 0.0241
Clinoferro- silite	2	0	0	1	0	9.754 (?) 0.0193	9.085 0.0110	5.243 0.0128	71.69 0.244	9.263 (?) 0.0214

(?) These values seem to show discrepancies.

In Table 4 there are some coefficients, b_{ip}, for which the standard deviations, s_{ip}, are greater than the coefficients themselves, thereby indicating that their values may not be significantly different from zero. A recalculation of regression coefficients after omitting these variables may give slightly improved values. But this slight improvement can never eliminate the major discrepancies noted. These discrepancies arise, because both the above-referred to regression equations (the first with five

TABLE 6. DIFFERENCES BETWEEN OBSERVED AND ESTIMATED UNIT CELL DIMENSIONS
$D = y(\text{obs.}) - y(\text{calc.})$.

Sp. No.	a Å	b Å	c Å	β°	$a \sin \beta$ Å
A	−.015	+.003	−.006	+.079	−.010
B	−.007	+.007	−.009	+.225	+.002
C	+.017	+.006	+.008	−.148	+.008
D	−.014	−.002	−.020	+.085	−.010
E	−.016	−.002	−.015	−.013	−.020
F	−.002	+.002	.000	−.062	−.006
G	+.002	+.006	−.003	+.009	.000
H	−.010	−.001	+.011	+.330	+.008
1	−.006	+.011	−.001	−.063	−.009
2	+.017	−.031	+.011	−.142	+.009
3	−.034	+.013	−.010	−.123	−.041
4	−.007	−.002	−.007	−.110	−.013
5	+.006	.000	+.013	−.040	+.003
6	—	−.001	—	—	+.012
7	—	+.001	—	—	+.007
8	+.039	−.001	+.010	+.409	+.048
9	+.010	+.006	−.001	+.039	+.010
10	+.007	+.010	−.008	+.178	+.018
11	+.006	−.008	+.009	−.195	−.001
12	+.002	−.002	−.008	+.215	+.016
13	+.018	+.006	+.011	−.014	+.014
14	+.005	−.011	+.006	−.279	−.013
15	−.006	+.008	−.001	−.033	−.004
16	−.004	−.003	−.002	−.017	−.004
17	−.007	−.015	+.011	−.330	−.024

variables and the second with 12 variables) are based on the assumption that the changes in the lattice constants, when the composition changes from $Mg_{50}Ca_{50}$ to $Fe_{50}Ca_{50}$, are equal to those when the composition changes from $Mg_{50}Fe_{50}$ to Fe_{100}. In the first case this change is equated to the influence of Mg^{2+} in B position (*i.e.*, X_3) and in the second case, this change is equated to the influence of Fe^{2+} in B position (*i.e.*, variable "x_6", Winchel's notation, 1961). On the other hand, as stated earlier, a change of composition from $Ca_{50}Mg_{50}$ to $Ca_{50}Fe_{50}$ causes a greater increase in $a \sin \beta$, a, β values than a change from $Mg_{50}Fe_{50}$ to Fe_{100}. It was also noted that the increase in $a \sin \beta$ is approximately three times. Even when all the cations are used as such as independent variables, (without assuming an ordered distribution) as done by Henriques (1958, a, b, c)

for optical properties, a linear regression equation cannot give a good correlation between cell dimensions and composition, because this equation is also based on the assumption that the effect of any individual cation (*e.g.*, substitution of Mg^{2+} by Fe^{2+}) on a particular dimension is always equal, *i.e.*, whether $Ca^{2+} = 0$ or $Ca^{2+} = 50$.

Thus a linear regression equation fails to give a satisfactory correlation
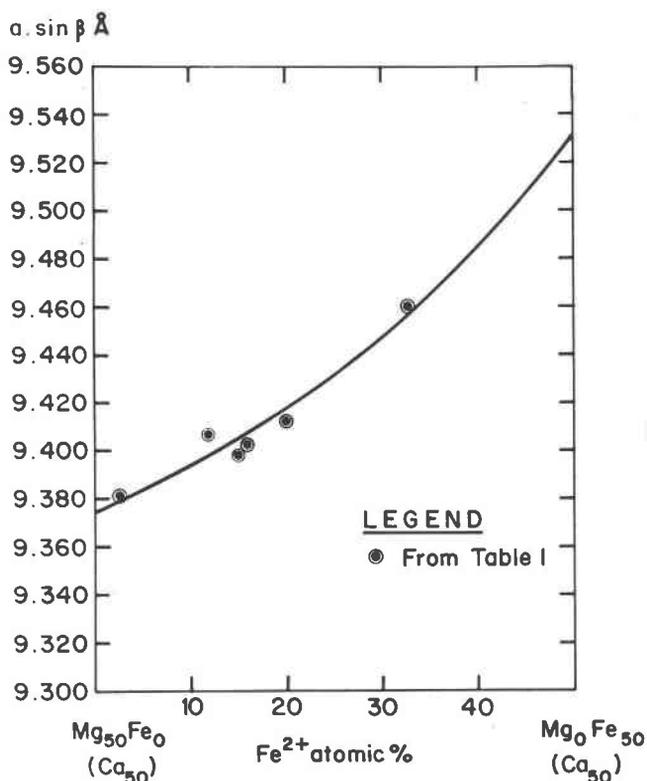
FIG. 2. Variation in the $a \sin \beta$ dimension of the clinopyroxene unit cell with $Mg^{2+} - Fe^{2+}$ substitution, Ca^{2+} remaining constant at the value 50.

between the lattice constants and the chemical composition; it means that the lattice constants, excepting perhaps the b dimension, of all the clinopyroxenes in the common clinopyroxene trapezium cannot be considered as linear, additive functions of the chemical composition; only in the clinoenstatite-clinoferrosilite series there are reasons to expect a linear variation. But linear regression equations appear to hold good for the refractive indices and specific gravity (Winchell, 1961). Perhaps these optical and physical properties are not very sensitive to the slight struc-

tural changes which exist between clinoenstatite-pigeonite-clinoferro-silite series and the diopside-hedenbergite series. But the lattice constants, especially a and β (consequently $a \sin \beta$) seem to be very sensitive to these structural changes and therefore the relation between them cannot be expressed satisfactorily by a linear equation. Recently even for the physical properties, Winchell (1963) has suggested the possibility of a discontinuity of a second order (*i.e.*, slope change) at $Mg_{50}Fe_{50}$ which, he attributes, to the ordered substitution of cations in A and B positions.
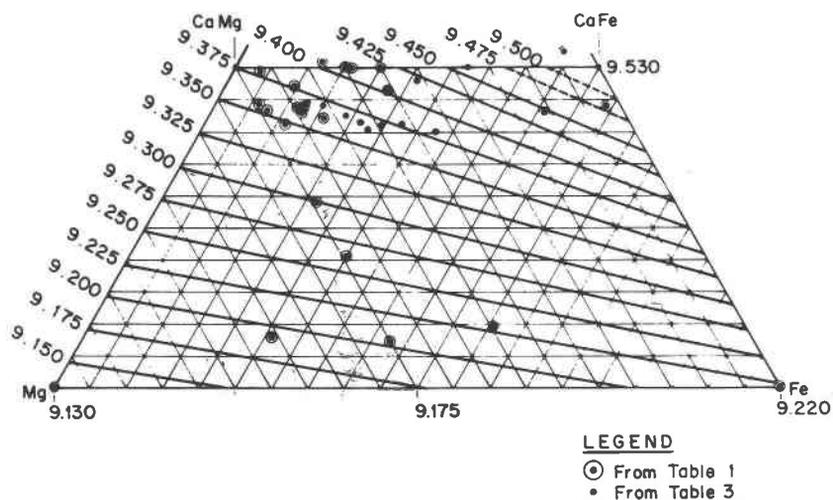
FIG. 3. Variation in $a \sin \beta$ throughout the common clinopyroxene trapezium. The isodimensional lines for values 9.475 Å and 9.500 Å are drawn as dashed lines.

Perhaps if second degree terms are also employed in the regression equations for lattice constants, there may be better agreement between observed and calculated values; but then the equation become so uncomfortably large and complicated (*e.g.*, the equations given by Henriques (1958c) for the refractive indices and 2V) that they cannot be looked upon as an elegant method of expressing the relationship. Perhaps the graphical method (Fig. 3) is simpler, though not very accurate and may satisfy the purposes of petrologists.

On the basis of the above observation that the changes in the lattice constants of the common clinopyroxenes are mainly due to the combined influence of Ca^{2+}, Mg^{2+} and Fe^{2+}, it was thought that a correlation diagram (Fig. 3) with reference to these three constituents, as suggested by Brown, will be very useful. This diagram is only a modification of that suggested by Brown. Of the five dimensions given in Tables 2 and 3,

$a \sin \beta$ and b were selected because these two can be more accurately determined from a powder photograph than the other three. Further there is an added advantage in using b dimension, because it shows almost a linear variation within the limits of experimental error. As stated earlier, the b values of clinoenstatite and clinoferrosilite, given by Brown, are in very good agreement with those of synthetic ones and hence, the isodimensional lines drawn by him (his Fig. 5) do not appear to need any revision. They can be drawn on this diagram (Fig. 3) for purposes of finding the composition of a pyroxene with the help of these two dimensions. In order to avoid confusion due to overcrowding of lines and to show better the variation in $a \sin \beta$ with the composition, the isodimensional lines for b are not drawn in Fig. 3. The lines for $a \sin \beta$ in this diagram have been drawn on the basis of the following:

1) A linear variation of $a \sin \beta$ with the composition has been assumed for the two component CaMg—Mg, Mg—Fe^{2+}, and CaFe—Fe^{2+} series of clinopyroxenes. Therefore these three sides of the trapezium have been divided into equal sections according to linear equations.

2) To get an idea of the variation of $a \sin \beta$ on the fourth side (CaFe-CaMg side), a graph, using the data of six pyroxenes, which have Ca^{2+} equal to or nearly equal to 50 atomic per cent, has been drawn (Fig. 2). In this graph also, a value of 9.530 Å has been assumed for $a \sin \beta$ of hedenbergite, $Ca_{50} Fe_{50}$.

3) A consideration of the $a \sin \beta$ values of all the pyroxenes plotted in this diagram. The pyroxenes (Table 3), whose compositions have been corrected for exsolution, have also been plotted in this figure.

4) Concidering the $a \sin \beta$ values of the three pyroxenes, which lie close to hedenbergite and considering the rapid increase in $a \sin \beta$ values near the hedenbergite-corner of the CaFe—CaMg side of the trapezium (see the steeply rising curve of $a \sin \beta$ in Fig. 2), the $a \sin \beta$ lines for values 9.475 Å and 9.500 Å are drawn as dotted lines. With some more data in this region of the trapezium it is possible to decide, whether they are really straight lines or slightly curved.

It must be noted that this diagram should be applied to only common clinopyroxenes, which contain constituents such as Fe_2O_3, Al_2O_3, MnO, Na_2O, K_2O, Li_2O, TiO_2 and Cr_2O_3 in minor amounts.

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