THE EFFECT OF ION SUBSTITUTION ON THE UNIT CELL DIMENSIONS OF THE COMMON CLINOPYROXENES

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Abstract

The unit-cell dimensions of eleven analyzed augites and ferroaugites from the Skaergaard intrusion are presented. The variation of the unit-cell dimensions b and $a \sin \beta$ is examined in relation to ion substitution, for the twenty-three analyzed common clinopyroxenes for which data are now available. For the three major substitution series, $Mg^{2+}:Fe^{2+}$, $Ca^{2+}:Fe^{2+}$ and $Ca^{2+}:Mg^{2+}$, the relationship between these two unit-cell dimensions and the ion substitution is regular, and linear equations are given for each series. The slope of the graph relating b-dimension to $Mg^{2+}:Fe^{2+}$ substitution is identical to that for the orthorhombic pyroxenes. The three series are combined in a triangular diagram relating unit-cell dimensions to $Ca^{2+}:Mg^{2+}:Fe^{2+}$ ratio, for the common clinopyroxene trapezium. The amount of substitution of Al^{3+} in octahedral coordination, and its effect on the b-cell dimension, is reconsidered.

Introduction

The fundamental pyroxene structure was determined in the case of diopside by Warren and Bragg (1929), while Warren and Biscoe (1931) later showed that hedenbergite and augite possessed a similar structure. The first attempt to study the changes in unit cell dimensions with ionic substitution in a group of pyroxenes (after a more general study by Ramberg and De Vore, 1951) was that of Hess (1952), who related the variation in a, b and c dimensions of the orthorhombic pyroxenes to substitution of Fe^{2+} for Mg^{2+}, and Al^{3+} for Mg^{2+} and Si^{4+}.

A beginning was made on the monoclinic pyroxenes by Kuno and Hess (1953) by determining the unit-cell dimensions of clinoenstatite, two pigeonites and three calcium-rich clinopyroxenes. A gradual change in unit cell dimensions throughout the main clinopyroxene trapezium (diopside—clinoenstatite—ferrosilite—hedenbergite) was tentatively suggested, and the degree of change was illustrated by sections across the field from diopside to hedenbergite, and from diopside to pigeonite. Kuno (1955) selected the diopside-pigeonite series for further detailed study, introducing four measured pyroxenes from the augite field which, together with the diopside and pigeonite used by Kuno and Hess, constituted a series of six pyroxenes showing the effect on unit-cell dimensions of the substitution of Fe^{2+} for Ca^{2+} (Mg^{2+} almost constant).

The effect of substitution of Fe^{2+} for Mg^{2+} was, so far, only illustrated in a general way by the three specimens studied by Kuno and Hess (1953, Fig. 5) which came from unrelated metamorphic rocks. The writer decided, therefore, to examine a series of chemically analyzed

clinopyroxenes from the Skaergaard intrusion, which showed continuous replacement of Mg^{2+} by Fe^{2+}, becoming almost complete, during the fractionation of a single body of basic magma, with Ca^{2+} varying only slightly between 35 and 45 atomic per cent, and with the minor cations showing hardly any variation. The greater part of this series has been described elsewhere in connection with their chemistry, optics and crystallization history (Brown, 1957), their specific magnetic susceptibility (Chevallier and Mathieu, 1958), and the magnetic moment of their contained ferrous ion (Chevallier and Martin, 1959).
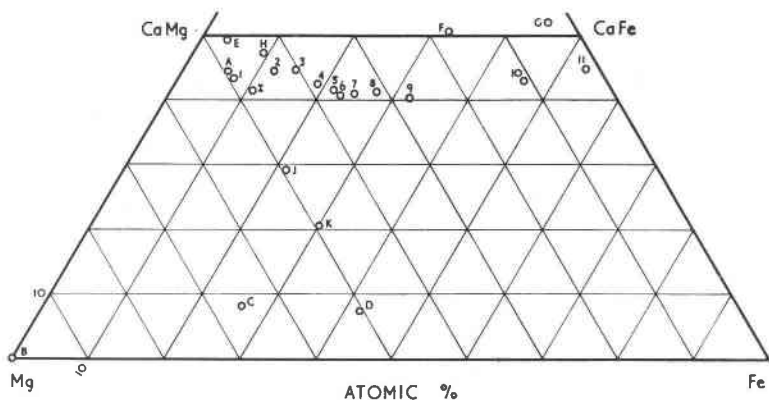

Fig. 1. The plotted points refer to chemically analyzed clinopyroxenes for which data on unit-cell dimensions are at present available. Points 1 to 11 refer to newly-measured Skaergaard specimens (corrected for exsolution), while points A to K refer to specimens described in previous literature. See Table 2 for further details.

Eleven measurements of unit-cell dimensions have been made of the Skaergaard pyroxenes, while at the same time one was made of a diopsidic pyroxene from Rhum (Brown, 1956, table 4). When the data for these twelve are considered in relation to the six of Kuno and Hess and the four of Kuno (with certain corrections made, see p. 17) several points of general significance emerge, quite apart from the effect of $Mg^{2+}:Fe^{2+}$ substitution. With data now available for twenty-two clinopyroxenes, it is possible to consider $Ca^{2+}:Fe^{2+}$ substitution (in relation to the problem of the character of the b-dimension change), $Ca^{2+}:Mg^{2+}$ substitution, and the effect of Al^{3+} in six-fold coordination. The information afforded by a knowledge of the three major substitutions, $Mg^{2+}:Fe^{2+}$, $Ca^{2+}:Fe^{2+}$, and $Ca^{2+}:Mg^{2+}$, make it possible to estimate, with some accuracy, the variation of cell-dimensions within the triangular diagram $Ca^{2+}:Mg^{2+}:Fe^{2+}$. It will be apparent, however, that

as a check more information is required for certain parts of even the common clinopyroxene field. This is also true of the ferrosilite region, although in view of the instability of these minerals at magmatic temperatures (Sahama and Torgeson, 1949), and the fact that if they crystallized stably at lower temperatures (e.g. metamorphic rocks) they will have subsequently inverted to the orthorhombic form, such information may not be forthcoming.

The twelve new measurements of the unit-cell dimensions were made on the same instrument used for the other ten by Kuno and Hess (the North American Philips X-ray diffractometer at Princeton University). This advantage simplified the author's work a great deal, for it was possible to relate and index the diffraction peaks by direct reference to the charts obtained by these two investigators.

IONIC-RATIO DETERMINATIONS

The commoner clinopyroxenes of igneous rocks vary chiefly in the relative proportions of the cations Ca^{2+}, Mg^{2+}, and Fe^{2+}. The effect of this variation on the unit-cell dimensions largely eclipses the effect of variation in the minor cations, apart from aluminum. Hence it is not practicable to discuss the effect in this series of the minor cations although ultimately it will be necessary for the effects of Ti, Na and Fe''' to be determined in those pyroxenes enriched in these elements. In the present study, particular attention has been paid to the manner in which the effects of Ca^{2+}, Mg^{2+}, Fe^{2+} and Al^{3+} can be estimated with fair accuracy.

In order to do this, with the commoner augites, two slight modifications to the methods of determination of ionic ratios used by Kuno and Hess (1953) and Kuno (1955) have been made. These concern the effect of exsolution on composition, and the meaning of the "Fe" co-ordinate in the Ca:Mg:Fe diagrams.

The Skaergaard clinopyroxenes have formed from a slowly-cooled body of magma, and many of those investigated show, as a result, evidence of having exsolved lamellae of calcium-poor pyroxene at subsolidus temperatures (Brown, 1957). These lamellae are subordinate to the host mineral, and are not believed (although evidence is desirable) to greatly affect the position of the reflection peaks of the host augite. If this is so, then the cell-dimensions determined are those of the host augite, while the chemical composition obtained from analysis is that of the host plus exsolved lamellae. So far, this problem has not affected the work of Kuno and Hess, who examined clinopyroxenes which were mostly from either volcanic or metamorphic rocks, and thus free from exsolved pyroxene. However, there is the risk that the determinative

diagrams presented in their paper will be applied directly to the commoner clinopyroxenes of plutonic rocks, which invariably contain exsolved pyroxene, with resultant errors. The Skaergaard suite of pyroxenes has therefore been corrected for exsolution to illustrate the need for this step and in this way can be used in conjunction with those from the other environments. The amount and identity of the exsolution (usually *ca.* 20% pigeonite) was determined, in each case, by optical and modal measurement, and the composition of the exsolved material assumed, in

TABLE 1. CHEMICAL ANALYSES OF THREE OF THE SKAERGAARD CLINOPYROXENES

(not previously published)

Wt. per cent	3	10	11	Atomic No. on basis of 6 oxygen atoms		3	10	11
SiO_2	50.82	48.18	46.90		Si^{4+}	1.908 ⎫	1.941 ⎫	1.928 ⎫
Al_2O_3	2.40	1.06	2.20	Z	Ti^{4+}	— ⎬ 1.999	0.008 ⎬ 2.000	— ⎬ 1.996
Fe_2O_3	1.88	1.46	1.66		Al^{3+}	0.091 ⎭	0.051 ⎭	0.068 ⎭
FeO	10.75	26.08	29.10		Ti^{4+}	0.025	0.013	0.002
MnO	0.19	0.53	0.67		Al^{3+}	0.015	—	0.038
MgO	14.36	3.52	0.58		Fe^{3+}	0.054	0.044	0.052
CaO	18.12	18.90	18.87		Cr^{3+}	0.002	—	—
Na_2O	0.39	0.23	0.32	WXY	Fe^{2+}	0.336 ⎫	0.879 ⎫	0.999 ⎫
K_2O	0.03	0.04	0.04		Mn^{2+}	0.007 ⎬ 2.001	0.019 ⎬ 2.001	0.022 ⎬ 2.009
TiO_2	0.96	0.70	0.10		Mg^{2+}	0.803	0.211	0.037
Cr_2O_3	0.06	n.d.	n.d.		Ca^{2+}	0.729	0.816	0.832
					Na^{1+}	0.029	0.017	0.025
					K^{1+}	0.001 ⎭	0.002 ⎭	0.002 ⎭
Total	99.96	100.70	100.44					

3. Augite from lower olivine gabbro, E.G.4389, Skaergaard intrusion, Anal. P. E. Brown.

10. Ferroaugite from ferrogabbro, E.G.4318, Skaergaard intrusion. Anal. E. A. Vincent.

11. Ferrohedenbergite from transgressive granophyre sill, E.G.4489, Skaergaard intrusion. Anal. E. A. Vincent.

each case, to be that of the co-existing calcium-poor pyroxene analyzed from the same, or an adjacent, rock. The errors inherent in such estimates are obvious, but fortunately slight errors do not affect the most important and dependable parameter for determinative diagrams, the *b*-cell dimension, which is little-affected by calcium-content (p. 29). The uncorrected analyses which are so far unpublished are given in Table 1. The rest of the uncorrected analyses, together with the composition of the exsolved phases used in the recalculations, and a description of the exsolution phenomena, are given in a previous paper (Brown, 1957). Once these corrections are made, the value of the initial, accurate chemical analysis is reduced. Sub-solidus exsolution, in fact, reduces the accuracy of a correlation between chemical composition and optical properties or unit-cell dimensions. A solution to this problem would seem

to be either homogenization by re-heating before making the physical measurements, or determination of the chemical composition of the host separately from that of the exsolved lamellae by, say, x-ray emission microspectroscopy.

The three major variables, in the common clinopyroxenes, are the divalent cations of Ca, Mg and Fe, and variation in cell-dimensions can be fairly-well related to these elements, and to some extent predicted from our knowledge of their ionic radii. The same cannot be said of minor cations such as Fe^{3+} and Mn^{2+}, although they have been grouped together with Fe^{2+} in the previous works by Kuno and Hess, obscuring the effect of any single cation replacement. This grouping would be al-right if Fe^{3+} and Mn^{2+} were almost identical to Fe^{2+} in ionic radius and structural site. While this may be the case for Mn^{2+}, it is not so for Fe^{3+}. The grouping together of Fe^{2+}, Fe^{3+} and Mn^{2+}, as single variable, is useful when contrasting the compositions of pyroxenes, particularly on a "molecular" basis, and was probably introduced for this purpose (Hess, 1949, p. 626). However, it is proposed here that the grouping be discontinued, together with the plotting of pyroxene compositions on a molecular Wo-En-Fs diagram, which introduces the same error, for Fs usually includes $Fe^{2+}+Fe^{3+}+Mn^{2+}$. It is nowadays usual to consider variation in isomorphous mineral groups in terms of ionic substitution, and the changes in optical properties (e.g. Hori, 1954 and 1956, and Ahrens 1958), as well as cell-dimensions, can be related to such substitution. The number of ionic substitutions involved in a group like the clinopyroxenes is such that it would be advantageous to isolate, ultimately, the effect of each variable cation on the mineral's physical properties; the grouping of cations under symbol headings (e.g. $Fe = Fe^{2+} + Fe^{3+} + Mn^{2+}$, or $Mg = Mg^{2+} + Ni^{2+}$, or $Ca = Ca^{2+} + Sr^{2+}$) is therefore a disadvantage for this purpose.

The pyroxenes under discussion have been examined for the effect of only the three major cations, Ca^{2+}, Mg^{2+} and Fe^{2+} (and to a lesser extent, Al^{3+}). The analyses of clinopyroxenes measured for cell-dimensions by Kuno and Hess have been recalculated to obtain the $Ca^{2+}:Mg^{2+}:Fe^{2+}$ percentage ratio in each case (Table 2). In one case (specimen G) this results in $Ca:Mg+Fe^{2+}$ exceeding 0.5. This is due to the large amount of Mn^{2+} ($MnO = 3.7\%$) substituting in octahedral co-ordination; only its inclusion with Fe^{2+} (or Mg^{2+}) in the ratio calculation will reduce the Ca% to the likely figure of 50% or less.

UNIT-CELL DIMENSION MEASUREMENTS OF SKAERGAARD PYROXENES

The pyroxene samples were powdered and mixed with acetone, and examined as a smear mount on a glass microscope slide. All measure-

TABLE 2. UNIT-CELL DIMENSIONS AND MAJOR VARIABLE CATION CONTENTS OF THE COMMONER CLINOPYROXENES

Specimen No.	Ca^{2+}	Mg^{2+}	Fe^{2+}	Al^{iv}	Al^{vi}	a Å	b Å	c Å	β	$a \sin\beta$ Å	Cell Volume Å³	Reference
1	43.4	49.1	7.5	0.099	0.040	9.746	8.910	5.268	73° 53′	9.363	439.6	Brown, 1957, No. 1
2	44.3	43.2	12.5	0.099	0.032	9.751	8.926	5.260	73° 57′	9.371	439.9	Brown, 1957, No. 3
3	44.6	40.3	15.1	0.096	0.015	9.753	8.928	5.259	73° 56′	9.373	440.0	Table 1, No. 3
4	42.3	38.7	19.0	0.084	0.018	9.754	8.940	5.270	73° 59′	9.375	441.7	Brown, 1957, No. 5
5	41.6	37.0	21.4	0.077	0.011	9.751	8.945	5.267	74° 02′	9.376	441.6	Brown, 1957, No. 6
6	40.5	36.5	23.0	0.086	0.019	9.753	8.944	5.267	74° 03′	9.378	441.7	Brown, 1957, No. 7
7	40.9	34.5	24.6	0.091	0.010	9.757	8.948	5.251	74° 06′	9.383	441.0	Brown, 1957, No. 8
8	41.0	31.4	27.6	0.058	—	9.758	8.954	5.255	74° 07′	9.385	441.5	Brown, 1957, No. 9
9	40.2	27.6	32.2	0.063	—	9.763	8.965	5.272	74° 13′	9.395	444.8	Brown, 1957, No. 10
10	42.8	11.1	46.1	0.051	—	(9.802)	9.004	(5.252)	(74° 45′)	9.457	(447.2)	Table 1, No. 10
11	44.5	2.0	53.5	0.068	0.038		9.024		[	9.486	—	Table 1, No. 11
A	44.3	49.6	6.1	0.094	0.051	9.734	8.907	5.246	73° 51′	9.350	436.9	Brown, 1956, table 4
B	—	100.0	—	—	—	9.618	8.828	5.186	71° 38½′	9.128	417.9	Kuno and Hess, 1953 No. 1
C	8.0	65.7	26.3	0.018	—	9.692	8.917	5.239	71° 27′	9.185	429.3	Kuno and Hess, 1953 No. 2
D	7.3	50.5	42.2	0.033	—	9.712	8.959	5.251	71° 27′	9.208	433.2	Kuno and Hess, 1953 No. 3
E	49.2	47.2	3.6	0.012	0.005	9.750	8.930	5.249	74° 10′	9.380	439.7	Kuno and Hess, 1953 No. 4
F	50.5	17.5	32.0	0.027	0.022	9.804	8.980	5.259	74° 46′	9.460	446.7	Kuno and Hess, 1953 No. 5
G	52.4	3.6	44.0	0.015	—	9.854	9.024	5.263	75° 40′	9.548	453.4	Kuno and Hess, 1953 No. 6
H	47.2	43.2	9.6	0.149	0.065	9.742	8.901	5.268	73° 55′	9.361	438.9	Kuno, 1955, No. 1
I	41.4	47.8	10.8	0.089	0.005	9.744	8.909	5.260	73° 28′	9.341	437.7	Kuno, 1955, No. 5
J	29.0	49.5	21.5	0.094	0.019	9.722	8.925	5.242	72° 57′	9.295	434.9	Kuno, 1955, No. 6
K	20.5	49.4	30.1	0.028	—	9.716	8.944	5.242	72° 20′	9.258	434.1	Kuno, 1955, No. 9

NOTES: (1) Specimens 1–11 are newly measured Skaergaard clinopyroxenes. Analyses corrected for exsolution in specimens 2–9 inclusive.
(2) Specimens A–K are measured clinopyroxenes in the literature, all apparently free from exsolution.
(3) Divalent cations expressed as a percentage of $Ca^{2+}+Mg^{2+}+Fe^{2+}$; in previous literature they have been expressed as a percentage of $Ca+Mg+Fe$ (where $Fe = Fe^{2+}+Mn^{2+}$).
(4) Aluminium expressed as number of atoms in 4-fold and 6-fold coordination, on the basis of a formula with 6 oxygen atoms.
(5) Values in parentheses are of doubtful accuracy and are not plotted.

ments were made with a North American Philips X-ray diffractometer using copper radiation at 35 kv and 15 ma.

A reconnaissance traverse was run on each sample at a scan speed of $\frac{1}{2}°$ 2θ per minute, the chart speed being such that $1°$ 2θ is represented by $\frac{1}{2}$ inch of chart paper. A range of 2θ from $93°$ to $28°$ was chosen, in order to locate the best peaks for measurement, and to assess their quality. As the measurements were done on the diffractometer at Princeton University, used earlier by Hess and Kuno (1953, 1955) for all the preceding studies of this type, on clinopyroxenes, the peaks were located and indexed by reference to the original, carefully indexed charts with the help of Professor Hess. The selected peaks were then examined individually at a slower scan speed of $\frac{1}{4}°$ 2θ per minute, so that $1°$ 2θ is represented by 1 inch of chart paper. Each peak was run six times, and the center could be established within $\pm 0.01°$.

The unit cell dimensions a, b and c, and β, were determined using the 2θ angles for the reflections from the following planes, in decreasing order of 2θ: $\{750\}$, $\{062\}$, $\{53\bar{1}\}$, $\{060\}$, $\{350\}$, $\{600\}$, $\{531\}$, $\{150\}$, $\{510\}$, $\{041\}$, $\{330\}$, $\{31\bar{1}\}$, $\{311\}$, $\{310\}$. An external standard of silicon powder mounted on a glass slide was used. For each run, the standard was introduced and reflection peaks obtained, from which a correction graph was constructed. Values for d were obtained using the value $\lambda\text{CuK}\alpha_1 = 1.54050$ Å.

The four most ferriferous pyroxenes (Nos. 8–11) were measured by Hess, Coleman and co-workers after the writer had returned to Oxford, and they reported (written communication 1/2/57) that the peaks became progressively poorer with increasing Fe content. The writer found that, with the magnesian members, only the peaks $\{750\}$ and $\{062\}$ were, at times, unusable, whereas Hess et al. found that with the ferriferous members only $\{531\}$, $\{53\bar{1}\}$ and $\{150\}$ were good peaks, $\{510\}$ fair, while $\{311\}$, $\{31\bar{1}\}$, $\{060\}$ and $\{600\}$ were poor but usable. As a check, the three good peaks were measured with iron radiation ($\lambda\text{FeK}\alpha_1 = 1.93597$ Å), and although the peaks were more ragged than with copper radiation, the 2θ values were larger and therefore allowed more accuracy. Hess (written communication 23/2/57) reported that with specimen numbers 10 and 11, the background was high, the peaks poor, and overlap of some peaks caused complications in $\{531\}$ and $\{53\bar{1}\}$. Thus the results for $a \sin \beta$ and b are consistent and believed dependable for the iron-rich members, whereas values for c, β and a are open to some doubt in specimens 10 and 11.

THE EFFECT OF ION SUBSTITUTION ON CELL-DIMENSIONS

The space group of diopside was determined as $C_{2h}{}^6\text{-}C2/c$ by Warren and Bragg (1929) while Warren and Biscoe (1931) showed that heden-

bergite and augite possessed a similar structure. Since then, the clino-pyroxenes have all been considered to have the diopside structure until Ito (1950) suggested, and Morimoto (1956) and Bown and Gay (1957) demonstrated, that monoclinic pyroxenes of the pigeonite group pos-sessed a space-group C_{2h}^5-$P2_1/c$. The likelihood of a solid-solubility gap between augite and pigeonite had earlier been demonstrated by Hess's (1941) description of the natural associations of clinopyroxenes, and their sub-solidus exsolution textures. Kuno (1955, p. 89) has shown that, ex-cept in rapid cooling, the pyroxenes of lavas fall into two groups, one with Ca^{2+} higher than 25%, and the other lower than 15%. Boyd and Schairer (1957, p. 33) find that, in the synthetic system $MgSiO_3$-$CaMgSi_2O_6$, the solvus intersects the solidus over a composition interval of about 15% (wt). They conclude that "homogeneous pyroxenes cannot exist stably in the composition interval between En40 (Di60) and En55 (Di45)," an interval corresponding to between Ca 30% and Ca 22% in the Ca:Mg:Fe diagram used by Kuno, and lying on the Ca-Mg join rather than within the Fe bearing field. Kuno's discovery (1955) of sub-calcic augites, however, suggests that supercooling may bridge the miscibility gap between stable pyroxene phases.

Despite this structural break, the cell-dimensions of augites and pigeonites are very similar (Kuno and Hess, 1953), and it is difficult at the moment to detect such a break, from any abrupt change in character of the cell-dimension curves across the pyroxene field. For the purposes of this account, therefore, the clinopyroxenes are considered as a single structural group.

In view of our knowledge of the diopside structure, some prediction can be made as to the particular cell-dimensions affected by certain cations, while a consideration of the relevant ionic radii indicates the probable magnitude of these effects. For example, the c-dimension is unlikely to be affected by changes other than Al^{3+} for Si^{4+} in the tetra-hedra of the chains aligned in this direction, whereas Ca^{2+}-Mg^{2+}-Fe^{2+} substitutions are likely to have their major effect on the a- and b-dimensions, and the angle β. In 6-fold coordination the ionic radii are $Ca^{2+} = 0.99$ Å, $Mg^{2+} = 0.66$ Å, $Fe^{2+} = 0.74$ Å (Ahrens, 1952), whereas the radius of Ca^{2+} in 8-fold coordination will be about 1.02 Å. Hence the change from augite to pigeonite should result in a marked decrease in a and b, whereas the change from diopside to hedenbergite ought to produce an increase (less marked) in a and b. Kuno and Hess (1953, fig. 5) have already shown that the latter increase does take place, Hess having earlier (1952) discussed it in more detail for orthopyroxenes, but the results of both Kuno and Hess (1953, Fig. 4) and Kuno (1955, Fig. 4) showed, somewhat unexpectedly, that the substitution of the large

Ca^{2+} by the much smaller Fe^{2+} ion resulted in an *increase* in the b-dimension (though a marked decrease in a). An attempt to analyze the cause of this has been made, by considering separately the effects on the b cell-dimension of the replacement of Ca^{2+} by Fe^{2+} and of Ca^{2+} by Mg^{2+}.

The substitution of Fe^{2+} for Mg^{2+} is fairly straightforward, and has the effect on b to be expected from the crystal chemistry. It is shown to be more regular than previously suggested, and this is therefore considered in some detail as an important diagnostic property for clinopyroxenes, as for orthopyroxenes.

The effect of Al^{3+} substitution in the octahedral position is considered separately from the effect of total Al^{3+} substitution in both tetrahedral and octahedral positions, and is shown to be unimportant in the common clinopyroxenes, only having a measurable effect on the b-dimension of one pyroxene so far determined.

In considering the cell-dimensions likely to be most critical in studying the major cation substitutions, attention has been focussed on two: the b-dimension and the value of $a \sin \beta$. The latter usefully combines the size of a and β and in this form indicates the spacing between (100) planes. The third dimension of the cell volume, c, is not yet believed dependable for diagnostic purposes, and the effect upon it of ionic subsitution cannot be demonstrated.

(a) *Substitution of Fe²⁺ for Mg²⁺*

As the common clinopyroxenes contain calcium as the third major divalent cation, $Mg^{2+}:Fe^{2+}$ substitution can only be examined by taking groups which lie on lines parallel to the base-line of the pyroxene trapezium, such as the pigeonite series or the diopside-hedenbergite series. However, detailed studies with full chemical analyses are rare in these compared with the commoner augite-ferroaugite series. So far, Kuno and Hess (1953, Fig. 5) have shown the general effect of $Mg^{2+}:Fe^{2+}$ replacement by plotting three members of the diopside-hedenbergite series, indicating that iron enrichment results in an increase in a, b and β, and has little effect on c. The increase is not linear, in the case considered, for any of the cell-dimensions. For the pigeonite series, figures for only two members have so far been published (Kuno and Hess, 1953, Table 1 and Kuno, 1955, Table 6); there is an additional figure by Morimoto (1956, p. 751) but this pigeonite has unfortunately not been chemically analyzed. With only two points available for the pigeonite series, and three for the diopside-hedenbergite series, the effect of substitution of Fe^{2+} for Mg^{2+} could not be evaluated with precision.

The eleven augites and ferroaugites measured from the Skaergaard intrusion all contain between 40 and 45% Ca (corrected for exsolution).

Taken together with the three diopside-hedenbergites studied by Kuno and Hess, a salite and an augite studied by Kuno (1955, Table 6, Nos. 1 and 5) and an augite studied by Brown (1956, Table 4), there are available chemical analyses and unit-cell dimensions of seventeen calcium-rich clinopyroxenes containing between 40% and 50% Ca. In addition there is the first member of the series to be measured, the diopside of Warren and Bragg (1929, p. 169). If the effect of $Mg^{2+}:Fe^{2+}$ replacement can be shown graphically for these eighteen clinopyroxenes, they then form a series comparable with the orthopyroxenes examined in this way by Hess (1952) and Kuno (1954), and a means exists for comparing ionic substitution in the orthorhombic and monoclinic pyroxenes.

The results cannot be plotted merely as an approximation to a series along the line, say, Ca 44%, because variation in calcium content from this mean figure will influence the iron percentage, desirable as the abcissa. As $Ca^{2+}/Ca^{2+}+Mg^{2+}+Fe^{2+}$ in the present samples averages 44%, however, the $Ca^{2+}:Mg^{2+}:Fe^{2+}$ ratios have been recalculated so that $Ca = 44$ in each case. In a graph showing changes in unit-cell dimensions with Fe^{2+} content, constructed for clinopyroxenes containing 44% Ca, those pyroxenes containing appreciably more or less than 44% Ca will be displaced from the ideal graph by an amount depending on the effect of Ca on the cell-dimension plotted. Fortunately, in the case of the b-dimension, which is of greatest significance in $Mg^{2+}:Fe^{2+}$ replacement, calcium has little effect (Fig. 5), and is negligible in the range $\pm 5\%$ Ca. In the $a \sin \beta$ graphs (Figs. 3 and 4), the effect is more marked and when changes in this dimension with $Mg^2:Fe^{2+}$ substitution were graphed (not shown), the series had to be divided into a 'high-calcium' (50%) and a 'low-calcium' (40%) group.

The b-dimension (Fig. 2) increases regularly, as Fe^{2+} substitutes for Mg^{2+} in the clinopyroxene structure. The increase is linear and can be expressed by the following equation:

$$b = 8.890 \text{ Å} + 0.00256(\text{Fe}) \text{ Å*} \tag{1}$$

where

$$\text{Fe} = 56Fe^{2+}/Mg^{2+} + Fe^{2+}$$

The most striking property of this equation is that the increment is the same as that obtained by Hess for the orthopyroxenes (1952, p. 176) in which

$$b = 8.805 \text{ Å} + 0.00255 (100 - \text{mg}) \text{ Å}$$

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* For the reasons stated by Yoder and Sahama (1957, p. 485), in such equations the independent variable should often be the spacing or cell-dimension, in which case this equation becomes:
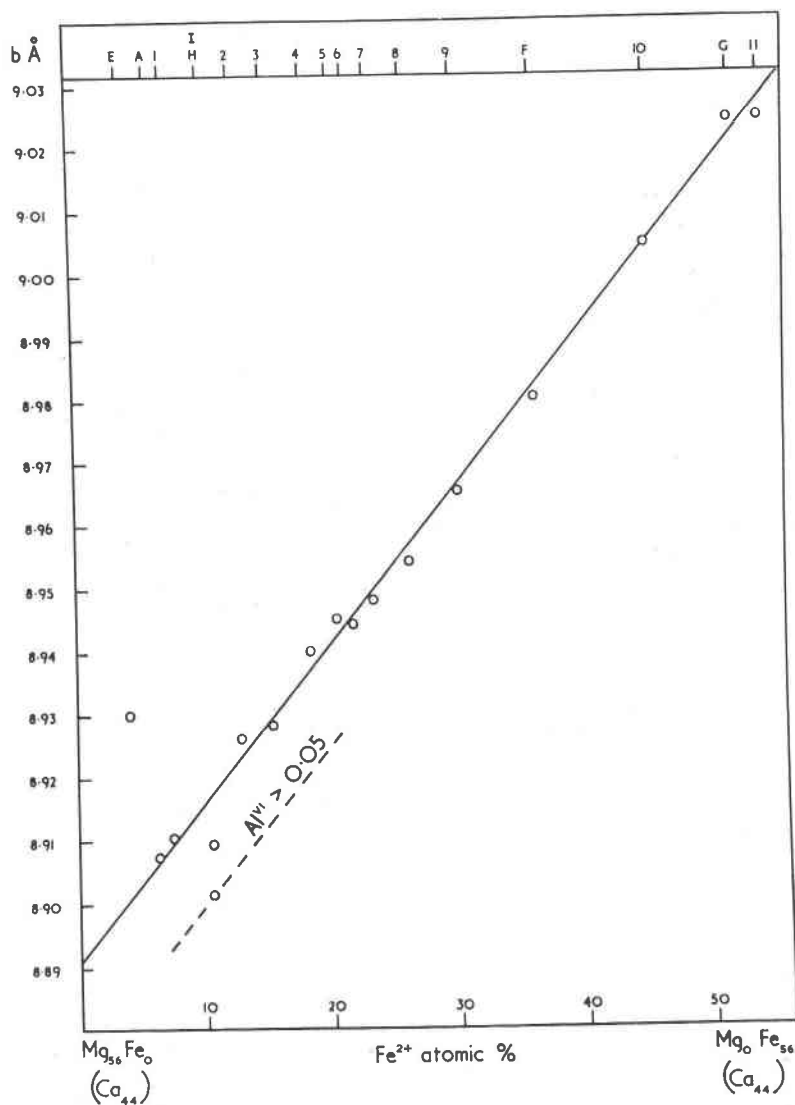
$$\text{Fe} = \frac{b}{.00256} - 3473$$

FIG. 2. Variation in the *b*-dimension of the clinopyroxene unit-cell, with $Mg^{2+}:Fe^{2+}$ substitution. The specimen numbers refer to those on Fig. 1 and in Table 2.

In the two equations, the factors (Fe) and (100-mg) mean the same thing, that is they represent the steadily increasing percentage of iron at the expense of magnesium, while the figures 8.890 Å and 8.805 Å represent the *b*-dimension of the magnesian end-members of the two

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series. The significant figure is the factor of 0.00256, which corresponds to the slope of the line. The identical nature of the increase in both monoclinic and orthorhombic pyroxenes emphasizes their similarity of structure, and the fact that in each series the iron and magnesium atoms are stacked along the b-axis.
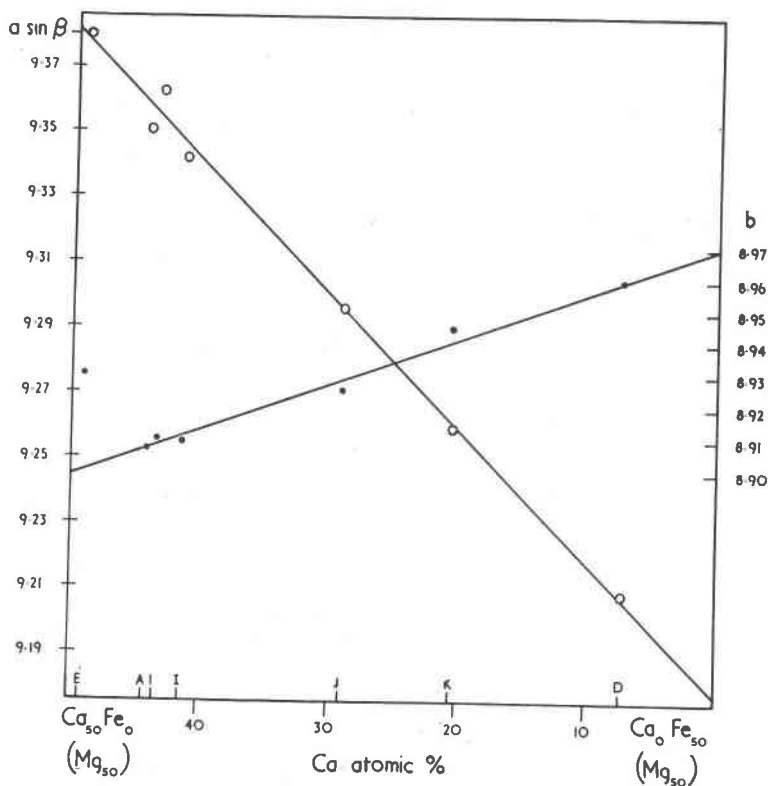
FIG. 3. Variation in b (dots) and a sin β (circles) with Ca^{2+}:Fe^{2+} substitution.

The regular identical increase in b for Mg^{2+}:Fe^{2+} substitution in both groups of pyroxenes makes it possible to estimate the b-dimensions of hedenbergite and ferrosilite, knowing those of diopside and clinoenstatite respectively, and the intermediate members of each series. Before doing this, however, a cross-check was made by establishing the nature of the changes in b from diopside to clinoenstatite and from hedenbergite to ferrosilite (see later), so that given a dependable figure for diopside, the values for the other three end-members could be estimated from more than one variable. Using Warren and Bragg's figure for almost pure diopside (1929, p. 169) of b = 8.89 Å, pure hedenbergite ought to have

$b = 9.018$ Å ($8.89 + 50 \times 0.00256$). However, as the main purpose of the present paper is to present curves and a determinative diagram for common clinopyroxenes, with average amounts of minor constituents, the values for the diopside corner of the trapezium are taken by extrapolation from the two linear series ($Mg^2 : Fe^{2+}$ and $Ca^{2+} : Fe^{2+}$) intersecting

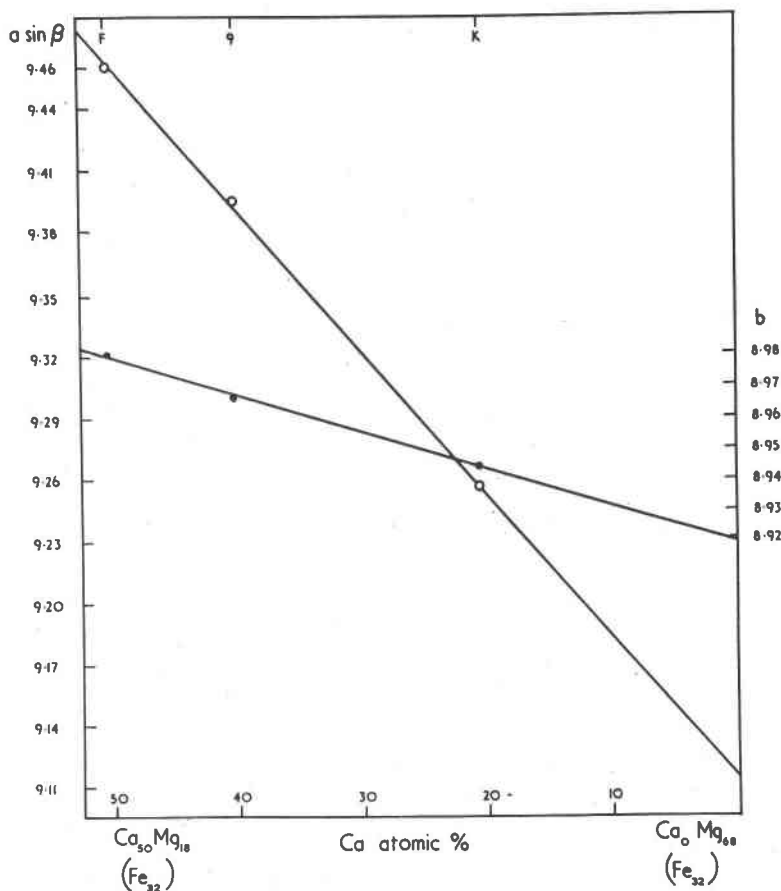FIG. 4. Variation b (dots) and $a \sin \beta$ (circles) with $Ca^{2+} : Mg^{2+}$ substitution.

at this corner (Fig. 2 being corrected so as to be appropriate for Ca 50, rather than Ca 44). Thus diopside has $b = 8.90$ Å (p. 29) and similarly hedenbergite has $b = 9.028$ Å, the latter being checked against the $Ca^{2+} : Mg^{2+}$ substitution series (p. 31).

The linear relationship discussed above is shown by fifteen of the pyroxenes (Fig. 2) within a band indicating a probable accuracy of ± 0.003 Å (equivalent, from the above equation, to $\pm 1\%$ Fe). Two

pyroxenes fall outside this band, the one falling below having an abnormally high Al^{3+} content (specimen H, Table 2). The pyroxene falling above the band, a skarn diopside (specimen E, Table 2) is comparable with many falling on the line in containing low amounts of Al^{3+}, Fe^{3+}, Ti^{4+} and Na^+. No satisfactory explanation can, at the moment, be offered for the anomalous b-dimension of this specimen.
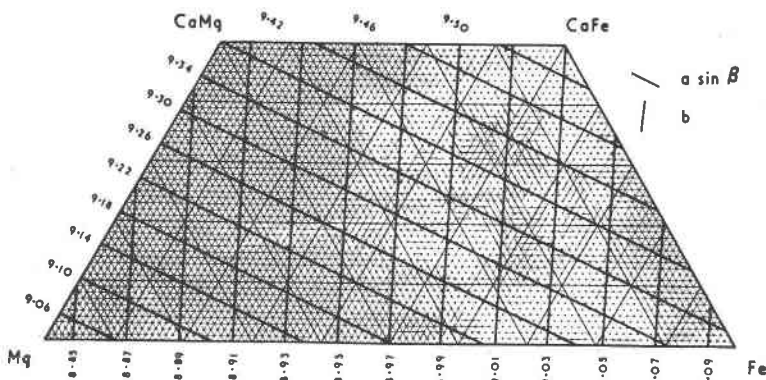
The $a \sin \beta$ dimension is too much affected by calcium-content to be

FIG. 5. Variation in b and $a \sin \beta$ throughout the common clinopyroxene trapezium. The lines are constructed on the basis of the results illustrated in Figs. 2, 3 and 4, and are only tentative in those parts of the field for which no data are available.

profitably illustrated on a $Mg^{2+}:Fe^{2+}$ substitution diagram. The effect of such substitution on $a \sin \beta$ can be seen, however, in Fig. 5, constructed from the other two substitution series involving calcium. The relationship is probably linear, as shown, and can be checked by taking groups with approximately equal calcium-content (e.g. specimens E and F, or I, 4 and 10, Table 2), although these are too rare and closely-spaced to be of much value.

The changes in c-dimension (Table 2) are not shown graphically as the plotted points show no pattern, possibly due to the difficulty of determining c. The c-dimensions of the Skaergaard series are consistently higher than the others, particularly in those members containing exsolved pigeonite $\|001$, and it is tentatively suggested that expansion along c may be related to this exsolution.

(b) *Substitution of Fe^{2+} for Ca^{2+}*

This type of substitution is demonstrated by examining a series of clinopyroxenes which lie on, or close to, a line parallel to the CaFe-Fe

side of the trapezium. A similar series has already been examined by Kuno (1955), the graphical representation of changes in cell-dimensions from diopside to pigeonite (loc. cit. Fig. 4) being a refinement of those shown by Kuno and Hess (1953, Fig. 4). The latter did not give β measurements, and therefore a and c values, for the series.

The reasons for re-considering this substitution are two-fold. Firstly, the curves of both Kuno and Hess, and Kuno, show the surprising result that the replacement of the large Ca^{2+} ion by the much smaller Fe^{2+} ion results in an *increase* in the b-dimension, though they did not comment upon this phenomenon. Secondly, the effect of Al^{3+} on the b-dimension was stressed, by constructing separate curves for pyroxenes high in Al^{3+}. The graphs for b, in each paper, are curved. As the present writer believes that the greater part of the Al^{3+} in these pyroxenes is in four-fold co-ordination, with little effect on the b-dimension, the graphs of Hess and Kuno have been re-drawn with this in mind. Anticipating that the change in b might prove to be linear, it was hoped that an examination of the regular change with $Ca^{2+}:Fe^{2+}$ substitution, compared with that for $Mg^{2+}:Fe^{2+}$ and $Ca^{2+}:Mg^{2+}$ substitution, would help to solve the problem of why b should increase with Fe^{2+} substitution for Ca^{2+}.

Two pyroxenes of the new series are introduced (from Skaergaard and Rhum) which, taken together with the three calcium-poor pyroxenes of Kuno and Hess, form a series (Fig. 1) on the line $Mg = 50\%$ ($\pm 1\%$). Two of the calcium-rich specimens previously plotted by Kuno (H and I, Table 2) are also included and, although they contain 43% and 48% Mg respectively, they clearly form part of the regular series. The St. Lawrence County diopside (E, Table 2) cannot be used, because of the high value for b (mentioned earlier (p. 28)).

The variation of b with $Ca^{2+}:Fe^{2+}$ substitution (Fig. 3) is clearly linear, and there is no doubt that this cell-dimension *increases* as iron substitutes for calcium. The change can be expressed by the equation:

$$b = 8.90 + 0.0014 \, (50 - Ca) \, A \tag{2}$$

where

$$Ca = \frac{100 \cdot Ca^{2+}}{Ca^{2+} + 50 + Fe^{2+}}$$

The points fall in a zone defining a probable accuracy of ± 0.003 Å. Extrapolation backwards indicates a figure for diopside of 8.90 Å (± 0.003 Å). If the value of 8.90 were replaced in this equation by the value for b of hedenbergite, then the equation would probably represent the changes in the hedenbergite-ferrosilite series (the same can be said of equation (3)). The total replacement of Ca^{2+} by Fe^{2+}, with Mg constant, results in an increase in b of 0.07 Å, so that in the calcium-free

clinoenstatite-ferrosilite series the clinopyroxene with a composition $Mg_{50}Fe_{50}$ should have a b-dimension of 8.97 Å.

The cause for the regular increase in b, as iron substitutes for calcium, remains to be considered. The Fe^{2+} ions cannot be directly substituting in the Ca^{2+} sites of the structure, or this would result in a decrease in b; nor can it be suggested that they are substituting without a shrinkage, for this would not explain the actual expansion observed. However, in passing from $Ca_{50}Mg_{50}$ to $Fe_{50}Mg_{50}$, the $Fe^{2+}:Mg^{2+}$ ratio increases. As will be shown in the next section in passing from $Ca_{50}Mg_{50}$ to Mg_{100}, b decreases by a small amount, but in passing from Mg_{100} to $Fe_{50}Mg_{50}$ b increases by about twice that amount. Thus the difference between this loss and gain must be made up in the passage from $Ca_{50}Mg_{50}$ to $Fe_{50}Mg_{50}$. In other words, the change in b is really governed by the change in the $Fe^{2+}:Mg^{2+}$ ratio, which increases in $Ca^{2+}:Fe^{2+}$ substitution because Mg^2 remains constant (the decrease in Ca^{2+} is reflected in the decrease in $a \sin \beta$).

This means that the substitution discussed in this section is not a simple one, as the substitution of Fe^{2+} for Mg^{2+} discussed earlier, where expansion of both $a \sin \beta$ and b took place. Here there has been a change in shape of the unit-cell with a decrease in $a \sin \beta$ and expansion along b. This change of structure would require more mobility of the ions than is necessary for the $Mg^{2+}:Fe^{2+}$ substitution. It is of interest, in this connection, to note that the series considered in this section includes a high-temperature assemblage of sub-calcic augites and pigeonite. The ionic mobility required for this type of structural change would be confined to the higher temperature range of crystallization, and the presence of a miscibility gap at lower temperatures (p. 22) understandable. This is in direct contrast to the augite and orthopyroxene series, in which the simple substitution of Fe^{2+} for Mg^{2+} results in complete isomorphous series at lower temperatures, given chemical fractionation under equilibrium conditions.

The $a \sin \beta$-dimension decreases regularly with substitution of Fe^{2+} for for Ca^{2+} (Fig. 3) and can be expressed by the linear equation:

$$a \sin \beta = 9.38 - 0.0040 \ (50 - Ca) \ \text{Å} \tag{3}$$

where

$$Ca = \frac{100 \cdot Ca^{2+}}{Ca^{2+} + 50 + Fe^{2+}}$$

The change in $a \sin \beta$ is marked, and indicates the importance of this dimension as a diagnostic parameter for the estimation of calcium-content in the clinopyroxenes. The change with total replacement of Ca^{2+}

by Fe^{2+} is 0.20 Å, so that $Mg_{50}Fe_{50}$ in the clinoenstatite-ferrosilite series would have $a \sin \beta = 9.18$ Å.

(c) *Substitution of Mg^{2+} for Ca^{2+}*

This substitution series falls on a line parallel to the CaMg-Mg side of the trapezium. There are not as many data available for this as for the other two series considered, but they suffice for the present purpose of establishing the general effect of this substitution compared with the other two. There are three clinopyroxenes which form a series parallel to the line $Fe = 31 \pm 1\%$ (specimens F, 9 and K, Table 2 and fig. 1), and a less useful series of three parallel to the line $Fe = 44 \pm 2\%$ (specimens G, 10 and D, Table 2 and fig. 1). Both series were used to determine the most probable slope of the graphs for in the case of both b and $a \sin \beta$ the two series fall on almost parallel straight lines, separated by an amount determined by their difference in iron content. In view of their similarity, only the graphs for the less ferriferous series have been reproduced (Fig. 4), as they serve to illustrate the points under consideration; the validity of the graphs and equations can be checked, if desired, by plotting the other series (Table 2).

The b-dimension decreases regularly with the substitution of Mg^{2+} for Ca^{2+}, in direct contrast with the increase shown by the substitution of Fe^{2+} for Ca^{2+}. The relationship is linear, and can be expressed by the equation:

$$b = 8.98 - 0.0012 \, (50 - Ca) \; \text{Å} \qquad (4)$$

where

$$Ca = \frac{100 \cdot Ca^{2+}}{Ca^{2+} + Mg^{2+} + 31}$$

This equation would be of more general application (as would equation (5)) if the figure of 8.98 were replaced by the b-dimension of either diopside (for the diopside-clinoenstatite series) or hedenbergite.

The total replacement of Ca^{2+} by Mg^{2+} results in a decrease in b of 0.06 Å, which is rather less than the increase of 0.07 Å for total replacement of Ca^{2+} by Fe^{2+} (equation (2)). Assuming a figure of $b = 9.028$ Å for hedenbergite, then the clinopyroxene $Mg_{50}Fe_{50}$ of the clinoenstatite-ferrosilite series would have $b = 8.968$ Å. From the $Ca^{2+}:Fe^{2+}$ substitution series, this latter clinopyroxene was expected to have $b = 8.970$ Å (p. 30). The fact that these two figures are almost identical is the best possible evidence for accepting the values obtained for the three substitution series.

The $a \sin \beta$ dimension decreases regularly, and most markedly, with

the substitution of Mg^{2+} for Ca^{2+} (Fig. 4). The change is again linear, and can be expressed by the equation:

$$a \sin \beta = 9.46 - 0.0070 \, (50 - Ca) \, A \qquad\qquad (5)$$

where

$$Ca = \frac{100 \cdot Ca^{2+}}{Ca^{2+} + Mg^{2+} + 31}$$

The total replacement of Ca^{2+} by Mg^{2+} would result in a decrease in $a \sin \beta$ of 0.35 Å. An independent figure for hedenbergite is not available, as the $Mg^{2+}:Fe^{2+}$ substitution series examined was not suitable for determining the linear variation in $a \sin \beta$. However, taking the figure for $Mg_{50}Fe_{50}$ of $a \sin \beta = 9.18$ Å obtained from the $Ca^{2+}:Fe^{2+}$ series (p. 31), hedenbergite ought to have $a \sin \beta = 9.53$ Å (the figure obtained by Kuno and Hess, 1953, Table 1, for a specimen close to hedenbergite, was $a \sin \beta = 9.55$ Å).

(d) *The effect of Al^{3+}*

For orthopyroxenes, Hess (1952) was able to demonstrate that a high Al_2O_3 content (in excess of $3\frac{1}{2}\%$) in two specimens produced a marked effect on the cell-dimensions, while the absence of Al_2O_3 from a pure enstatite produced a similar, but opposite effect. The substitution of the smaller Al^{3+} for Mg^{2+} or Fe^{2+} in the octahedral positions resulted in a decrease in b, while the substitution of small amounts of the larger Al^{3+} for Si^{4+} in the tetrahedral position resulted in a slight increase in c. Kuno (1954, Fig. 2) showed a similar effect of Al^{iv} on c, but the curve for b corresponding to a high Al^{vi} content is more appropriate for his specimens (Nos. 11 and 13) containing hardly any Al^{vi}.

For clinopyroxenes, Kuno and Hess indicated (1953, fig. 4) that for three of the specimens plotted (I, J and K of Table 2) a high Al^{3+} content decreased b, compared with the other two specimens (D and E of Table 2). Kuno (1955, fig. 4) also indicated this effect, as shown by three specimens (H, I and J of Table 2), noting also that the high Al^{3+} of two of them resulted in an increase in the c-dimension.

The effect of Al^{3+} on the b-dimension of the clinopyroxenes has been reconsidered in the present study, and although it is believed to be as significant, in theory, as suggested by the previous investigators, only one specimen among the twenty-two so far measured appears to contain enough Al^{3+} in six-fold coordination for its effect to be observed. Hess (1952, p. 177) showed why entry of Al^{3+} in six-fold coordination, and not four-fold coordination, would shorten the b-dimension of orthopyroxenes, but in later work on the clinopyroxenes both Kuno and Hess considered only the effect of *total* Al^{3+} on the b-dimension. In the three specimens

shown to contain much more than 0.05 Al^{3+} atoms to 6 oxygen atoms, as revealed by the chemical analyses, the greater part of this aluminium appears to be substituting for Si^{4+} in the tetrahedral position (Kuno, 1955, Table 1, nos. 1, 5 and 6). Of the eleven Skaergaard clinopyroxenes, none contains more than 0.05 Al^{3+} atoms to six oxygens, in six-fold coordination (judging from the recalculation of the analyses, Table 2), although some contain as much as 0.139 total Al^{3+} atoms. Thus, the only clinopyroxene which contains a little more than average aluminium in the octahedral position is the salite from a eucrite block in Taga volcano (Kuno, Table 1, no. 1), which contains 0.065 Al^{3+} atoms to six oxygens, as compared with 0.040 in the most extreme example from the Skaergaard series.

The plot of b-dimensions in Figs. 2, 3 and 4 shows that the majority of the specimens form a linear series. One which falls well off the line is the salite mentioned above (specimen H of Fig. 2), which indicates that although much variation in Al^{3+} content below 0.05 is tolerated without change in b, once this critical amount is exceeded a reduction in b is observed. The diopside from St. Lawrence County also falls well off the line. The reason for this specimen's high b value is not understood; it cannot be attributed to its low Al^{3+} content, as many Skaergaard examples appear to contain none at all in six-fold coordination.

The effect of Al^{3+} on c has not been considered in this account, in view of the unreliability of the new c-values, but in view of the high proportion of Al^{3+} appearing to substitute for Si^{4+} in the more calcic clinopyroxenes (cf. Wilkinson, 1957, p. 128, and Table 3) it is likely that the "abnormal" curves for c will be those for low Al^{3+}, rather than for high Al^{3+} content.

The Determination of Ca:Mg:Fe Ratio from the Unit-Cell Dimensions

The commoner clinopyroxenes, such as those considered in this paper, contain only minor amounts of elements such as Fe^{3+}, Na^+ and Ti^{4+}, and the estimation of their composition from physical properties is based on correlation of these properties with the $Ca^{2+}:Mg^{2+}:Fe^{2+}$ ratio of the mineral. The present study of the three major substitution series makes it possible to estimate the variation of the unit-cell dimensions, b and $a \sin \beta$, with complete substitution of the three major variable cations. This is simplified by the linear variation in these two cell-dimensions (within the present limits of accuracy) with ionic substitution.

A preliminary diagram relating the cell-dimensions of clinopyroxenes to composition has been given by Kuno and Hess (1953, Fig. 6), outlining a general pattern for the variation which is confirmed by the present study. The present diagram (Fig. 5), however, differs from that of Kuno

and Hess in several features which are largely refinements based on the extra data now available. The cell-dimensions chosen for the graph are b and $a \sin \beta$, rather than b and a. Both β and c were recorded as points, rather than curves, by Kuno and Hess; the plotting of $a \sin \beta$ usefully combines the changes in a and β, while the changes in c are too slight and irregular to be of much value at present. The second change in the new diagram is that, whereas the a and b lines of Kuno and Hess were curved, irregularly spaced and non-parallel, the present set are straight, evenly-spaced and parallel. Finally, the values for b and $a \sin \beta$ of the end-members of the trapezium CaMg-Mg-Fe-CaFe are slightly different in the present diagram.

The isodimensional lines for b were constructed as follows. Firstly, the values for hedenbergite, clinoenstatite and ferrosilite were obtained, accepting the value of $b = 8.900$ Å for diopside. From the $Mg^{2+} : Fe^{2+}$ substitution series (p. 27), hedenbergite would have $b = 8.900 + 0.128 = 9.028$ Å. From the $Ca^{2+} : Fe^{2+}$ substitution series (p. 29) ferrosilite would have $b = 9.028 + 0.07 = 9.098$ Å, while $Mg_{50}Fe_{50}$ would have $b = 8.900 + 0.07 = 8.970$ Å. From the $Ca^{2+} : Mg^{2+}$ substitution series (p. 31) clinoenstatite would have $b = 8.900 - 0.06 = 8.84$ Å, while $Mg_{50}Fe_{50}$ would have $b = 9.028 - 0.06 = 8.968$ Å. From the $Mg^{2+} : Fe^{2+}$ substitution series, ferrosilite would have $b = 8.84 + 0.256 = 9.096$ Å.

Given the values for the four corners of the trapezium, and the linear equations for $Mg^{2+} : Fe^{2+}$ substitution, the diopside-hedenbergite and clinoenstatite-ferrosilite series can be sub-divided into equal units and joined by the isodimensional lines shown in Fig. 5. As the incremental change of b with $Mg^{2+} : Fe^{2+}$ substitution (and constant Ca^{2+}) appears to be the same throughout, regardless of actual calcium content, the lines cannot be curved and irregularly spaced but must be straight, parallel, and equidistant. The slant towards the Mg side of the field is a reflection of the slight difference in total change of b in the $Ca^{2+} : Fe^2$ series ($+0.07$) compared with the $Ca^{2+} : Mg^{2+}$ series (-0.06). If these were identical (0.065), then the b lines would run vertically down the field.

The isodimensional lines for $a \sin \beta$ were constructed in a somewhat similar way. Accepting a figure for diopside of $a \sin \beta = 9.38$ Å (Fig. 3), then from the $Ca^{2+} : Fe^{2+}$ substitution series $Mg_{50}Fe_{50}$ would have $a \sin \beta = 9.38 - 0.20 = 9.18$ Å. From the $Ca^{2+} : Mg^{2+}$ substitution series, $Ca_{50}Fe_{50}$ would have $a \sin \beta = 9.18 + 0.35 = 9.53$ Å, while Mg_{100} would have $a \sin \beta = 9.38 - 0.35 = 9.03$ Å. From the $Ca^{2+} : Fe^{2+}$ series ferrosilite would have $a \sin \beta = 9.53 - 0.20 = 9.33$ Å. In view of the lack of a linear equation for the $Mg^{2+} : Fe^{2+}$ series, cross-checks are not applicable in this case, and given more data the $a \sin \beta$ curves might ultimately be refined. Nevertheless, the linear relationships for the other two substitution series make

it possible to construct the isodimensional lines with little difficulty. Thus the CaMg-Mg and CaFe-Fe sides of the trapezium can be divided into equal sections according to the linear equations, and straight, parallel, equidistant lines drawn. Again, it is not possible to meet the require- ments of these two equations by drawing curved and irregularly-spaced lines.

The values obtained in Fig. 5 pose a problem in connection with the cell dimensions of clinoenstatite. From the diagram, it would appear to have $b = 8.84$ Å, $a \sin \beta = 9.03$ Å. Kuno and Hess (1953) obtained values for synthetic clinoenstatite, of $b = 8.83$ Å, $a \sin \beta = 9.13$ Å (Specimen B, Table 2), while Atlas (1952) obtained values of $b = 8.86$ Å, $a \sin \beta = 9.11$ Å. By the method used in this paper, of examining ion substitution series and extrapolating, it is difficult to arrive at a figure for $a \sin \beta$ approaching 9.13 Å. On the other hand, naturally-occurring clinopyroxenes have been used for the present study, and the values obtained for the clinoenstatite- ferrosilite series relate to somewhat hypothetical minerals, conveniently regarded as end-members of the natural series which, for direct compari- son, would have had to crystallize under natural magmatic or metamor- phic conditions and contain similar amounts of the minor cations.

CONCLUSIONS

There are now sufficient data, from the x-ray measurements of twenty- three analyzed clinopyroxenes, to estimate with some accuracy the effect on the unit-cell dimensions b and $a \sin \beta$ of substitution of Fe^{2+} for Mg^{2+}, Fe^{2+} for Ca^{2+}, and Mg^{2+} for Ca^{2+}, and to be more sure of the effect of Al^{3+} substitution in the octahedral lattice-sites of the structure. This stage is a necessary preliminary to any further studies on the effect of other cations such as Fe^{3+}, Ti^{4+}, Na^+ or Li^+.

The substitution of Fe^{2+} for Mg^{2+} results in a regular increase in b, and an increase which is probably regular in $a \sin \beta$ and unit-cell volume. The increase in b is linear, and the increment for each atom substituted (as expressed by the linear equation) is identical with that for the orthopyroxenes. This regularity may account for the fact that $Mg^{2+}:Fe^{2+}$ substitution is dominant and continuous in both series during crystal fractionation. The regularity is at variance with Ramberg and De Vore's (1951) findings, but in view of Sahama and Torgeson's (1949) thermo- chemical studies, it is believed that complete solid solution exists in the orthopyroxene series.

The substitution of Fe^{2+} for Ca^{2+} results in a regular increase in b and decrease in $a \sin \beta$, both changes being expressible in linear equations. The linear relationship suggests complete solid solution throughout the series, which may be explicable on the grounds that the specimens cor-

sidered include sub-calcic augites which may have crystallized meta-stably owing to quick-cooling from a high temperature. The increase in b is difficult to explain by simple substitution of the smaller Fe^{2+} for Ca^{2+} and may indicate greater ionic mobility in this higher-temperature series. The structural change attendant upon an increase in b and decrease in $a \sin \beta$ may not be possible with stable crystallization at lower tempera-tures and would help to explain the miscibility gap in this compositional range, in plutonic rocks. The absence of a break in the linear series ex-amined is of interest in view of the slight differences which exist between the structure of augite and pigeonite (see p. 22).

The substitution of Mg^{2+} for Ca^{2+} results in a regular decrease in b, $a \sin \beta$ and unit-cell volume, the latter decrease being of a high order.

The incorporation of Al^{3+} in octahedral sites results in a slight decrease in b. However, this effect is only shown by one of the 23 clinopyroxenes so far measured, the rest containing so little Al^{3+} in this position that it has no measurable effect on the b or $a \sin \beta$ unit-cell dimensions. The distinc-tion made between Al^{3+} in six-fold coordination and total Al^{3+} is the chief reason why the graphs shown here are linear and differ from the curves shown by previous investigators.

The effects on unit-cell dimensions of the three major ionic substitu-tions in the commoner clinopyroxenes can be combined in the pyroxene part of the $CaSiO_3$-$MgSiO_3$-$FeSiO_3$ triangular diagram (Fig. 5), and the diagram used to estimate composition from measured values for b and $a \sin \beta$. In this connection, the remarks made earlier (p. 17) on the ef-fect of sub-solidus exsolution and the minor cations should be borne in mind.

The results incorporated in Fig. 5 might ultimately be used to elucidate some of the problems associated with the role of the clinopyroxenes in petrogenesis, when more is known about the stability of certain structures at different temperatures. The implication would be that in a particular magma certain pyroxene structures would form at particular tempera-tures, and with cooling the magma would become progressively depleted in the particular cation assemblage which could fit easily into these struc-tures. Thus the trend of compositional change followed by the Skaer-gaard pyroxenes (Brown, 1957, Fig. 2) is initially one which shows no change in $a \sin \beta$. If, at a lower temperature, the $a \sin \beta$ dimension can expand, then the structure can incorporate more calcium and the direc-tion of the trend will change (Muir, 1951, Fig. 1). This type of change has often been attributed to factors such as a decrease in the aluminium con-tent of the magma so that less feldspar crystallizes and the clinopyroxene *must* take the surplus calcium into its structure. This implies that the magma chemistry influences structural changes in the minerals, whereas

it is suggested here that the physical conditions might influence the structural changes which, in turn, affect the magma chemistry.

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