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UNIT-CELL DIMENSIONS OF SOME ALUMINOUS NATURAL CLINOPYROXENES

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ABSTRACT

Newly computed unit-cell dimensions of nine salites and augites containing between 0.11 and 0.26 atoms of Al per six oxygen atoms, and varying amounts of Fe^{3+} and Ti, are compared with the cell dimensions of clinopyroxenes containing lesser amounts of these minor constituents. High total Al can be correlated with reductions in the *b* and *a* sinβ parameters. Al in six-fold coordination, Fe^{3+} and Ti, may each give some reduction in *b*, but there is no distinct correlation between the total $Al^{VI}+Fe^{3+}+Ti$ and the reduction in *b* and *a* sinβ. The amount of Al in four-fold coordination can be correlated very well with an increase in the *c*-dimension.

INTRODUCTION

The relationship between chemical composition and unit-cell parameters of the natural clinopyroxenes within the field diopside-clinoenstatite-ferrosilite-hedenbergite have been investigated by Kuno and Hess (1953), Kuno (1955) and Brown (1960). Kuno and Hess drew a tentative diagram showing variations in cell dimensions for the whole of the clinopyroxene field based on six specimens from igenous and metamorphic rocks. With data determined for eleven clinopyroxenes from the Skaergaard intrusion, Brown (1960) examined in detail the variation of the unit-cell parameters, *b* and *a* sin β, in relation to ion-substitution for the twenty-three common clinopyroxenes for which data were then available, and drew a determinative diagram for the common clinopyroxenes with relatively small amounts of minor constituents.

Salitic clinopyroxenes analysed during the course of investigating the mineralogy of some ejected plutonic blocks from the Soufrière volcano, St. Vincent, West Indies, were found to contain between 4.78 and 5.98 percent Al_2O_3 but otherwise show a small range in chemical composition (Table 1, Nos. 1–4). As this is considerably more than that reported for most natural clinopyroxenes, the unit-cell dimensions of these clinopyroxenes have been compared with those containing lesser amounts. The associated mineral phases, in each of the blocks from which the clinopyroxenes were separated, are listed in order of abundance in the key to Table 1. Analysis No. 5 in Table 1 is of an augite containing comparatively low amounts of Al, Fe^{3+} and Ti separated from a norite ejected block.

In addition Dr. R. W. Le Maitre kindly made available small amounts of the clinopyroxenes analysed by him from the Gough Island alkaline

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volcanics. These clinopyroxene analyses are included in Table 1, and have previously been published by Le Maitre (1962, 1965). Two specimens, G50 and G15, are similar in composition to the St. Vincent salites except for their higher Ti content.

The St. Vincent clinopyroxenes are very fresh, with very weak zoning, whereas the Gough Island clinopyroxenes are slightly zoned. Exsolution lamellae are absent from the clinopyroxenes examined optically, and only the one pyroxene phase has been found from the X-ray diffractometer studies.

This study forms part of a detailed mineralogical and petrological study of the ejected plutonic blocks collected by the late Professor L. R. Wager in 1959 from the Soufrière, St. Vincent. The blocks are regarded as igneous crystal cumulates (Wager, 1962). Further papers dealing with aspects of the mineralogy of other mineral phases, and the petrology of the plutonic blocks, will be published separately.

X-RAY METHODS

The determinations of the unit-cell dimensions *a*, *b*, *c* and β were made on the mineral powders using a Phillips X-ray diffractometer. Cu$K\alpha$ radiation at 35 kV and 15 mA was used. Reconnaissance scans were run at $\frac{1}{2}°2\theta$/min; accurate measurements at $\frac{1}{4}°2\theta$/min. The divergence and scatter slits were 1°.

The mineral powders were mounted as thin smears on a glass slide, using the following method. The mineral sample, together with silicon as standard, was finely ground under acetone and the resulting suspension transferred, using a dropper, onto a glass slide within an area previously marked out with a wax crayon. As the acetone evaporated, a drop of acetone celluloid solution was added and mixed in with the drying mineral suspension. The addition of celluloid gives a much more even surface than if acteone alone is used. The smears were just translucent, and any thick preparations were rejected. Samples were prepared in triplicate and scans made of each. Silicon was used as both an internal and external standard. It was found essential to use interval standards for the most accurate work.

The centers of each peak were established by using dividers at $\frac{3}{4}$ of the peak height. Measurements of 2θ were made to $\pm 0.005°$ or better with a rule graduated to 0.01 mm. The reproducibility for the 2θ measurements in triplicate was found to be better than $\pm 0.01°$.

The unit cell parameters *a*, *b*, *c*, β and cell volume were determined using the 2θ angles for the reflections from the following planes, in increasing order of 2θ: 021, 220, 221, 310, 311, 131, 112, 002, $22\bar{1}$, $31\bar{1}$, 330, 041, 510, 150, 531, 600, 350, 060, $53\bar{1}$.

TABLE 1. CHEMICAL ANALYSES OF CLINOPYROXENES FROM ST. VINCENT, WEST INDIES AND GOUGH ISLAND, SOUTH ATLANTIC

	Sample No.	1 SV1	2 SV2	3 SV3	4 SV4	5 SV5	6 G30S	7 G121	8 G50	9 G15
	SiO_2	48.73	49.27	49.44	49.48	50.64	49.25	51.05	49.74	49.53
	TiO_2	0.81	0.81	0.78	0.86	0.57	1.52	1.30	2.02	1.78
	Al_2O_3	5.98	5.34	5.08	4.78	2.54	5.26	4.46	4.12	4.29
	Fe_2O_3	2.47	2.56	2.65	2.54	2.36	2.27	1.28	1.14	1.43
	Cr_2O_3	0.05	n.d.	n.d.	n.d.	n.d.	—	—	—	—
	FeO	4.96	5.08	5.19	5.31	8.57	6.40	4.87	6.17	6.71
	MnO	0.15	0.18	0.17	0.19	0.39	n.d.	n.d.	0.15	0.16
	MgO	14.43	14.62	14.58	14.62	14.51	15.08	15.89	14.83	14.66
	CaO	22.49	22.17	21.82	21.80	19.75	19.14	21.04	21.34	20.52
	Na_2O	0.26	0.25	0.26	0.24	0.52	0.78	0.44	0.54	0.55
	K_2O	0.0008	0.0008	0.0009	0.0008	n.d.	0.05	0.09	0.07	0.06
	H_2O^+	0.00	n.d.	n.d.	0.00	n.d.	0.04	—	—	—
	Total	100.33	100.18	99.97	99.82	99.85	99.79	100.42	100.12	99.69
		Cations on a basis of 6 oxygens								
Z	Si	1.803	1.822	1.833	1.838	1.898	1.827	1.865	1.843	1.844
	Al^{IV}	0.197	0.178	0.167	0.162	0.101	0.173	0.135	0.157	0.156
WXY	Al^{VI}	0.063	0.055	0.054	0.047	0.010	0.057	0.058	0.021	0.032
	Ti	0.022	0.022	0.022	0.024	0.016	0.042	0.035	0.056	0.049
	Fe^{+3}	0.069	0.071	0.074	0.071	0.067	0.063	0.035	0.031	0.040
	Cr	0.001	—	—	—	—	—	—	—	—
	Mg	0.796	0.806	0.805	0.808	0.810	0.834	0.870	0.825	0.820
	Fe^{+2}	0.153	0.157	0.161	0.165	0.269	0.199	0.149	0.191	0.208
	Mn	0.005	0.005	0.005	0.005	0.012	—	—	0.004	0.004
	Ca	0.891	0.878	0.866	0.867	0.793	0.761	0.822	0.847	0.818
	Na	0.019	0.018	0.018	0.017	0.038	0.056	0.031	0.040	0.040
	K	—	—	—	—	—	0.002	0.004	0.004	0.004
	Z	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
	WXY	2.02	2.01	2.01	2.01	2.01	2.01	2.00	2.02	2.02
	Ca	46.8	45.8	45.3	45.2	40.7	41	44	45	43
	Mg	41.8	42.0	42.1	42.2	41.5	45	46	43	44
	Fe	11.4	12.2	12.6	12.6	17.8	14	10	12	13
	% Al in Z	9.9	8.9	8.4	8.1	5.1	8.8	6.7	7.9	7.8
	α	1.690	—	—	1.691	—				
	β	1.697	1.697	1.697	1.697	1.697				
	γ	1.716	—	—	1.717	—				
	Range in β	± 0.001	± 0.001	± 0.001	± 0.001	± 0.002				
	ZAC	43°	—	—	43°	43°				
	$2V_z$	57°	56°	56°	56°	52°−51°				
	Sp.Gr.	3.36	—	—	3.36	—				

Key

Samples 1–5 from the St. Vincent ejected blocks.

(1) No. 1. Salite from plagioclase (An_{94})-olivine (Fo_{76})-salite-amphibole-magnetite cumulate (T770).
No. 2. Salite from plagioclase ($An_{93.5}$)-olivine (Fo_{74})-salite-amphibole-magnetite cumulate (T896).
No. 3. Salite from plagioclase (An_{93})-olivine (Fo_{72})-salite-magnetite cumulate (T774M).
No. 4. Salite from plagioclase (An_{90})-olivine (Fo_{70})-salite-magnetite-amphibole cumulate (T748A).
No. 5. Augite from norite (T731C) (non-accumulative).

Analyst J. F. Lewis

(2) Samples 6–9 from the Gough Island volcanics (Le Maitre, 1962; 1965)
No. 6. Augite from xenolith.
No. 7. Diopsidic augite phenocrysts; picrite basalt.
No. 8. Titanaugite phenocrysts; trachybasalt.
No. 9. Titanaugite phenocrysts; trachybasalt.

Analyst R. W. Le Maitre

TABLE 2. DUPLICATE UNIT-CELL MEASUREMENTS ON SKAERGAARD AUGITE, IN Å

	a	*b*	*c*	*β*	Cell volume Å^3
Brown (1960, Table 2, No. 2)	9.751	8.926	5.260	73°57′	439.9
Lewis (duplicate measurement)	9.754	8.926	5.262	73°95′	440.3

Indexing was carried out by reference to the chart of an indexed Skaergaard endiopside, through the courtesy of Dr. G. M. Brown, and by reference to the paper of Kuno and Hess (1953). The cell parameters were calculated using a least-squares method with the aid of the Oxford University Mercury digital computer. The cell parameters for the St. Vincent clinopyroxenes are believed to be accurate to within ±0.002 Å. The reflections on the diffractometer traces for the Gough samples were not as sharp as those from St. Vincent and the cell parameters for these samples are estimated to be accurate to within ±0.003 Å.

In order to test the accuracy and reproducibility of the X-ray results, a Skaergaard augite sample, measured by Dr. G. M. Brown when at Princeton University, was run simultaneously with some of the writer's samples. Table 2 gives the results obtained by Dr. Brown for the Skaergaard augite and also those obtained by the writer for the same sample. It is seen that whilst the measurements for the *b*-dimensions are identical, there is a slight discrepancy in the *a*- and *c*-dimension measurements.

TABLE 3. UNIT-CELL DIMENSIONS OF CLINOPYROXENES FROM ST. VINCENT AND GOUGH ISLAND

	Sample	Ca^{2+}	Mg^{2+}	Fe^{2+}	*a*Å	*b*Å	*c*Å	*β*°	*a* sin *β*	Cell volume Å^3
1	SV1	48.4	43.3	8.3	9.738	8.896	5.271	73.93	9.358	438.7
2	SV2	47.7	43.8	8.5	9.747	8.905	5.274	73.86	9.364	439.8
3	SV3	47.3	43.9	8.8	9.749	8.907	5.274	73.83	9.364	439.8
4	SV4	47.0	44.0	9.0	9.749	8.908	5.274	73.83	9.364	439.8
5	SV5	42.3	43.3	14.4	9.749	8.924	5.263	73.71	9.357	439.5
6	G30S	44.6	47.3	8.1	9.733	8.898	5.277	73.67	9.340	438.5
7	G121	42.3	46.7	11.0	9.746	8.910	5.263	73.56	9.347	438.8
8	G50	45.5	44.3	10.3	9.742	8.902	5.273	73.86	9.359	439.3
9	G15	44.3	44.4	11.3	9.748	8.904	5.277	73.64	9.353	439.4

Notes (1) Samples 1–5, St. Vincent. Analyses given in Table 1.
(2) Samples 6–9, Gough Island alkaline volcanics. Analyses given in Table 1.

However, these differences are within the limits of experimental error and the results can be considered very satisfactory for the present purposes.

RESULTS AND COMPARISONS

The unit-cell parameters determined in the present study are listed in Table 3. The compositions in terms of the Ca:Mg:Fe^{2+} ratios are also given. The numbers of atoms substituting in octahedral and tetrahedral sites, as calculated from the chemical analyses on the basis of six oxygen atoms, are also given for ready reference (Table 4).

Unit-cell dimension b. Using the data for the eleven analyses of augites and ferroaugites from the Skaergaard intrusion together with the data for the calcic clinopyroxenes studied by Kuno and Hess (1953), Brown (1960) showed that there was considerable sensitivity of the *b*-dimension to changes in the Mg:Fe^{2+} ratio, for clinopyroxenes having a Ca:Mg+Fe ratio of between 40 and 50 percent. The *b*-dimension is hardly affected by variation over a range of 10 percent Ca. A linear relationship was established for fifteen clinopyroxenes in the series $Ca_{44}Mg_{56}Fe_0$-$Ca_{44}Mg_0Fe_{56}$. Two clinopyroxenes plotted at some distance from the line, these being a skarn diopside from St. Lawrence Co. and a salite from the Taga eucrite bomb. No explanation could be offered for the former, which plotted above the line. The low *b*-dimension of the Taga salite was attributed by Brown to the high quantity of Al substituting in octahedral positions.

The Ca:Mg:Fe^{2+} ratios of the clinopyroxenes examined here (Table 3) have been recalculated so that the %Ca=44 in each case, and the data plotted on the diagram of Brown (1960, Fig. 2), correlating the *b*-dimension with change in the Mg:Fe^{2+} composition ratio (Fig. 1). It is seen that the *b*-dimensions of the St. Vincent salites (SV1-SV4) plot below the line, together with that of the salite from the Taga eucrite bomb and also the augite No. 5 of Kuno (1955). All these clinopyroxene samples, except Kuno's No. 5, have high Al and Fe^{3+} contents compared with those falling on the line (here termed the linear series). The Gough Island samples, which contain considerable amounts of Al and Ti, also plot below the line except for sample G121. This sample, together with sample SV5, which contains low amounts of Al, Ti and Fe^{3+}, plots on the curve.

Unit-cell dimension c. Kuno and Hess (1953) and Kuno (1955) correlated the higher *c*-dimension values obtained for some of their samples with high *total* Al contents. Hess (1952) considered that in orthopyroxenes the substitution of Al^{IV} for Si at first increases the *c*-value, but larger

TABLE 4. NUMBERS OF ATOMS IN FOUR-FOLD AND SIX-FOLD CO-ORDINATION (BASED ON SIX OXYGEN ATOMS) FOR ENDIOPSIDES, AUGITES AND SALITES FOR WHICH CELL PARAMETERS HAVE BEEN DETERMINED

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Sample No.	SV1	SV2	SV3	SV4	T.E.	H.K.	G30S	G121	G50	G15	Rh	Sk1	Sk2	Sk3	Sk4	SV5
Al^{IV}	0.197	0.178	1.167	0.162	0.149	0.089	0.173	0.135	0.157	0.156	0.098	0.099	0.097	0.091	0.081	0.101
Al^{VI}	.063	.055	.054	.047	.065	.005	.057	.058	.021	.032	.049	.040	.030	0.15	.015	.010
$Fe^{(+3)VI}$	.069	.071	.074	.071	.058	.027	.063	.035	.031	.040	.015	.042	.047	.054	.038	.067
Ti^{VI}	.022	.022	.022	.024	.022	.022	.042	.035	.056	.049	.013	.027	.022	.025	.036	.016
$Tot.^{VI}$	.154	.148	.150	.142	.145	.054	.162	.128	.108	.121	.077	.109	.096	.094	.089	.093
$Cr^{(+3)VI}$	.001	—	—	—	—	—	—	—	—	—	.026	.013	.004	.002	—	—

Nos. 1-4 St. Vincent salites (Table 1, Nos. 1-4).
No. 5 Salite from Taga eucrite bomb (Kuno, 1955, No. 1).
No. 6 Phenocryst from andesite (Kuno, 1955, No. 5).
Nos. 7–10 Gough Island clinopyroxenes (Table 1, Nos. 6–9).
Nos. 11–15 Samples forming linear series for *b*-dimension. Specimens A, 1, 2, 3 and 4 of Brown (1960, Table 2)
No. 16 Augite from norite block, St. Vincent (Table 1, No. 5).

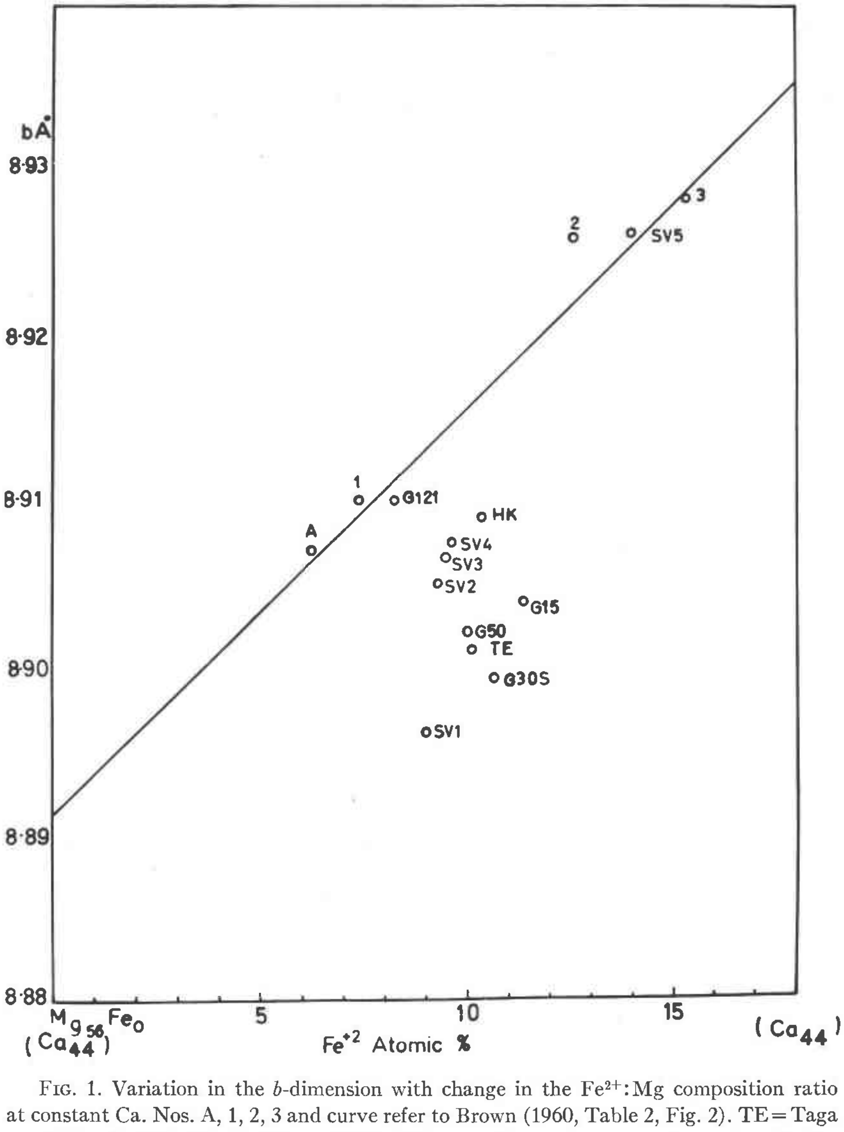

FIG. 1. Variation in the b-dimension with change in the Fe^{2+}:Mg composition ratio at constant Ca. Nos. A, 1, 2, 3 and curve refer to Brown (1960, Table 2, Fig. 2). TE = Taga eucrite bomb; HK = No. 5 of Kuno (1955). Others are the newly-measured samples—Tables 2 and 3.

amounts cause the (Si, Al)O_3 chains to zig-zag in the (010) plane and no further increase in c would occur.

Brown (1960), with more data available, found no significant pattern in variation of the c-dimension. He considered that this was possibly related to the difficulty in determining *c* with the accuracy needed to detect the slight variations to be expected. However, he noted that the *c*-dimensions of the Skaergaard clinopyroxenes were consistently higher than the others measured, and tentatively suggested that this may be due to exsolution of pigeonite ||001.

In Figure 2 the *c*-dimensions of the clinopyroxenes have been plotted against variation in the Mg: Fe^{2+} composition ratio. It is seen that despite considerable scattering the plots of the St. Vincent salites and Gough Island samples (except G121), together with the Taga eucrite bomb sample, are consistently higher than all others plotted. Sample G121 and the clinopyroxene from the norite SV5 have lower *c*-values, similar to those of the Skaergaard clinopyroxenes.

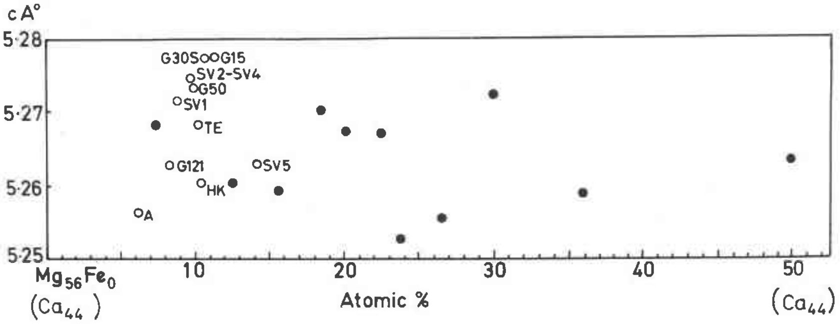

FIG. 2. Variation in the *c*-dimension with change in the Fe^{2+}:Mg composition ratio at constant Ca. ○ Labelled as for Figure 1. ● Clinopyroxenes from the Skaergaard intrusion (Brown, 1960).

Unit-cell parameter a *sin β*. The preliminary work by Kuno and Hess (1953) and Kuno (1955) indicated that there was an increase in the *a*-dimension on passing from diopside to hedenbergite (i.e. with Mg⇌Fe replacement). In the series diopside-ferropigeonite, however, a very marked decrease was found with decrease in Ca content. The parameter $a \sin \beta$ is more useful since it measures d_{100}. Brown (1960) showed that $a \sin \beta$ varied mainly with Ca content, but also changed slightly with variation in Fe^{2+} and Mg. Brown's data show that the parameter $a \sin \beta$ is extremely sensitive to variation in Ca content. A change in $a \sin \beta$ of 0.01 Å corresponds to change in Ca content of approximately 1.5 percent as read from the determinative graph (Brown, 1960, Fig. 5, p. 28).

The $a \sin \beta$ values obtained for the samples in this study are best compared with those previously studied using the determinative graph constructed by Brown (1960, Fig. 5, p. 28). It is found that the measured values for the St. Vincent salites and G30S are approximately 0.025 Å lower than indicated by the graph. All these samples have greater than 1.5 atoms Al per six oxygens. The $a \sin \beta$ values for the Gough Island samples G50 and G15 are lower by approximately 0.015 Å. Samples G121 and SV5 also give lower measured values than those indicated by the graph, but the discrepancy is less than 0.01 Å.

Although there is this marked reduction in $a \sin \beta$ for the samples investigated here, the salites from St. Vincent, except SV1 (which has the highest Al content), have higher $a \sin \beta$ values than the Gough Island samples. This corresponds with the higher Ca content of the St. Vincent salites.

DISCUSSION

The highly substituted natural clinopyroxenes studied here, containing considerable amounts of Al, Fe^{3+} and Ti, show a reduction in the $a \sin \beta$ and b parameters and increase in the c parameter when compared with natural clinopyroxenes containing lesser amounts of these constituents.

Sakata (1957), Clark *et al* (1962), and Coleman (1963) have shown that the addition of alumina to diopside results in a decrease in a, b, $a \sin \beta$ and the cell volume, while c increases. Assuming that equal numbers of atoms replace Mg and Si in six-fold and four-fold co-ordination respectively, these are the results to be expected since the replacement of Mg(0.66 Å)[1] by the smaller Al(0.51 Å) should decrease a and b, whereas substitution for Si (0.40 Å) in the tetrahedral positions should increase the c-dimension.

Using synthetic materials, Coleman (1963) has also investigated the effect of the additions of small amounts of Fe, Ti, Cr and other elements besides Al on the unit-cell dimensions of diopside. He found that substitution of the type $Fe^{3+}Al^{3+}$ for $Mg^{2+}Si^{4+}$ resulted in a decrease in b and an increase in c. a, β and $a \sin \beta$ remained practically constant. Substitution of the type $Ti^{4+}Al_2^{3+}$ for $Mg^{2+}Si_2^{4+}$ resulted in a decrease in b and β, whilst a and c increased and $a \sin \beta$ remained constant.

There is a good overall correlation between the *total* amount of Al present and the reduction in the b-dimension in the samples investigated here with the exception of sample G121 and Kuno's specimen No. 5. This feature is in agreement with the views of Kuno and Hess (1953) and Kuno (1955). However, this does not take into account the site of substitution.

Calculation of the chemical anaylses on the basis of six oxygen atoms,

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[1] Ionic radii taken from Ahrens (1952) and Green (1959).

and making the Z group equal to 2 by the addition of Al, indicates that most of the Al in the clinopyroxenes investigated probably occurs in the tetrahedral sites, and that Fe^{3+} and Ti substitute in octahedral sites together with the remainder of the Al. Substitution of Al for Si in tetrahedral sites should cause an increase in the *c*-dimension, and this is the effect observed in the natural clinopyroxenes studied here. All clinopyroxenes with a Ca content of between 40 and 50 percent, and containing more than 1.5 atoms of Al per six oxygen atoms in four-fold coordination, show an increase in the *c*-dimension. These samples also show a decrease in the *b*-dimension. The magnesian Skaergaard clinopyroxenes, sample No. 5 of Kuno (1955), G121 and SV5, contain less than 1.5 atoms per six oxygen atoms in four-fold coordination and have lower *c*-dimensions. The fact that SV1 has the largest amount of Al in four-fold coordination, and yet has a slightly lower *c*-dimension than the other St. Vincent salites, suggests that some factor, in addition to the Al content, is influencing the *c*-dimension.

None of the samples which form the linear series for the *b*-dimensions has more than 0.05 atoms of Al in six-fold coordination. However, the amount of Al in six-fold coordination, in the samples showing a decrease in *b*, is not much greater than, and in some cases is less than, those samples forming the linear series.

The St. Vincent salites contain between 0.06 and 0.07 atoms of Al per six oxygens atoms in six-fold coordination and this should contribute towards the reduction in the *b*-dimension. No. 5 of Kuno (1955), and G50 and G15, however, contain only 0.005, 0.02 and 0.03 atoms of Al respectively, which is less than that in some of the samples forming the linear series. G121 contains a greater amount of Al in six-fold coordination than the other Gough Island samples, and yet there is no reduction in *b* for this sample. However, G121 contains the least amount of Al in four-fold coordination for the Gough Island samples.

Substitution of Fe^{3+} in octahedral sites should result in a small decrease in *b*, as the results of Coleman (1963) have shown. The St. Vincent salites contain greater amounts of Fe^{3+} than the Skaergaard samples, and this should be a contributing factor towards a decrease in *b* for these particular samples. The amount of Fe^{3+} in the Gough Island samples is similar to that of the Skaergaard samples, except for G30S which contains considerable Fe^{3+} (0.062 atoms).

G30S, G50 and G15 contain more than 0.04 atoms of Ti per six oxygen atoms. None of the other samples contains as much as this, and most contain only 0.02 atoms. The role of Ti in ionic substitution will depend upon its valency, which cannot be determined by chemical analyses in the presence of Fe. If Ti is present as Ti^{4+} in octahedral sites there should be a decrease in *b*, since the ionic radius (0.68 Å) is smaller than that of Fe^{2+} (0.74 Å).

Verhoogen (1962) considered that, in the presence of Fe, Ti is more likely to occur in octahedral sites as Ti^{3+}, which has an ionic radius of 0.76 Å. If this is so, the effect on the unit-cell would be small and may even increase *b*, assuming that Ti is substituting for both Fe^{2+} and Mg. However, the results of Coleman's experiments indicate a decrease in *b* with substitution of Ti for Mg. Hence, it seems probable that the greater amounts of Ti in the Gough Island samples may have contributed to the observed decrease in *b*.

A reduction in $a \sin \beta$ has also been observed in relation to curves constructed for pyroxenes with low amounts of Al, Ti and Fe^{3+}. The greatest reduction in this parameter is found in samples SV1 and G30S, which can be correlated with the fact that these two contain the most Al, in both four-fold and six-fold coordination. This is also in accordance with the observed reductions in $a \sin \beta$ with the addition of Al to diopside in the synthetic experiments. However, samples G50 and G15, which contain comparatively small amounts of Al in six-fold coordination, also show a reduction in $a \sin \beta$, although to a lesser degree than the St. Vincent salites. Coleman (1963) found no reduction in $a \sin \beta$ with the addition of Fe^{3+} and Ti^{4+}. This suggests either that Coleman's data are not applicable to the natural iron-bearing pyroxenes, or that the distribution of Al is not in accordance with that assumed here.

According to the ionic radii and the experimental data, Al^{3+} substituting in octahedral positions should give the greatest observed reduction in *b* and $a \sin \beta$. Fe^{3+} should also give a reduction in *b* but to a lesser extent, and Ti^{4+} possibly gives a reduction in *b*. Examination of Table 4 shows that, although all the samples showing a decrease in *b* have higher contents of total $Al+Fe^{3+}+Ti$ in six-fold coordination (except for No. 5 of Kuno, 1955), the two Gough Island samples G50 and G15 have contents hardly greater than for some of the samples forming the linear series. The effect of Cr should not be neglected and appreciable quantities (>1000 ppm) were reported by Le Maitre (1962) for the Gough Island samples. These were determined spectrographically and have not been assessed here.

CONCLUSIONS

A reduction in the *b* and $a \sin \beta$ parameters and an increase in the *c* parameter has been observed for the highly substituted clinopyroxenes studied here compared with those containing lesser amounts of minor constituents. High total Al and high Al in four-fold coordination correlate with reduction in the *b* and $a \sin \beta$ parameters and increase in *c*.

Substitution of the smaller ions, particularly Al in octahedral positions, should cause a reduction in b and $a \sin \beta$. It does in the St. Vincent salites but the distinction is not so clear for the Gough samples and for No. 5 of Kuno (1955).

Al, Fe^{3+} and Ti substituting in octahedral positions may each give some reduction in b, but there is no distinct correlation between the total $Al^{VI}+Fe^{3+}+Ti$ and the reduction in b and $a \sin \beta$. These apparent discrepancies might be due to analytical error but might also result from wrong assumptions on the distribution of the ions and the valency of Ti. Similar anomalies can been seen from the data on orthopyroxenes presented by Howie (1963). Further studies on clinopyroxenes from different environments and showing variation in ionic substitution, *e.g.* omphacitic clinopyroxenes compared with fassaites, should give more information on these problems.

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