STUDY OF ORTHOPYROXENES FROM VOLCANIC ROCKS

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Abstract

Orthopyroxenes from volcanic rocks covering a composition range from bronzite to eulite were studied and the result is compared with the properties of orthopyroxenes from plutonic and metamorphic rocks. Orthopyroxenes crystallized at high temperatures contain from 0.104 to 0.057 Ca in atomic proportion, whereas those crystallized at low temperatures contain less than 0.033 Ca. Pleochroism appears to depend on Ti content. The volcanic orthopyroxenes having compositions about $Mg:Fe^{+2}+Fe^{+3}+Mn=1:1$ show optic angles (2V about X) 7° larger than those of the plutonic and metamorphic rocks. This departure gradually diminishes as the composition becomes either more magnesian or more ferriferous. Unit cell dimensions a, b, and c all increase with Fe^{+2} substituting for Mg. But the a and c dimensions increase more markedly with Ca substituting for Mg than with Fe^{+2}. Aluminum substituting for Mg causes contraction of the b dimension.

Introduction

Orthopyroxenes from volcanic rocks have been less studied than those from plutonic and metamorphic rocks, chiefly because of the difficulty of obtaining pure materials for analysis owing to their fine granularity, close association with clinopyroxenes, and abundance of minute inclusions. However, in orthopyroxenes from plutonic and metamorphic rocks, most of the Ca which was originally contained in the crystals has been exsolved to form lamellae, resulting in the orthopyroxenes of the Bushveld type (Hess and Phillips, 1938). Exsolution of Ti to form ilmenite lamellae was found by Sugi (1951) in diallage, and exsolution blebs or rods of sphene were also described by Hess (1949) in ferrosalite from metamorphic and plutonic rocks. Thin ilmenite lamellae in some orthopyroxenes were probably formed by exsolution. Therefore the plutonic and metamorphic orthopyroxenes have a very narrow range of Ca and perhaps Ti contents after slow cooling and complete adjustment of equilibrium. The volcanic orthopyroxenes have a wider range of Ca, its amount depending on the temperature of crystallization. The effect of Ca on the physical properties of orthopyroxenes can be determined from the study of the volcanic orthopyroxenes.

The result of the present study offers a method for determining the Ca content in orthopyroxenes. The Ca content may be used as a geothermometer.

Another difficulty attached to the study of the volcanic orthopyroxenes is their strong zoning. The writer has never seen unzoned pyroxenes from volcanic rocks. In order to make correlation between the optical constants and the chemical composition of the same specimen, we should determine the exact range of the optical constants and take the mean

values. However, the variation of physical constants with Fe^{+2} content can be known more exactly by studying unzoned pyroxenes from plutonic and metamorphic rocks. This study has been made by Hess (1952).

The writer's study has not yet been completed because of the lack of analyses of ferrohypersthene and eulite (the nomenclature by Poldervaart, 1947) from volcanic rocks. But in view of the difficulty of obtaining such data in the near future, the writer intends to publish the results so far obtained.

The present paper includes 13 analyses of the volcanic orthopyroxenes and 6 analyses of the plutonic and metamorphic orthopyroxenes. Only one of them has not been examined by the writer (eulite from Manchuria described by Tsuru and Henry, 1937). To complete the curves showing the variation of 2V and unit cell dimensions, several unanalyzed pyroxenes were also studied.

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CHEMICAL COMPOSITIONS

The analyses of orthopyroxenes are given in Table 1. The modes of occurrence and localities are shown in Tables 3 and 4, respectively, in which those of unanalyzed pyroxenes are also included.

The general formula for pyroxenes may be written as follows (Hess, 1949):

$$(W)_{1-p}(X, Y)_{1+p}Z_2O_6$$
$$W = Ca^{+2}, Na^{+1}, K^{+1}$$
$$X = Mg^{+2}, Fe^{+2}, Mn^{+2}, Ni^{+2}$$
$$Y = Al^{+3}, Fe^{+3}, Cr^{+3}, Ti^{+4}$$
$$Z = Si^{+4}, Al^{+3}$$
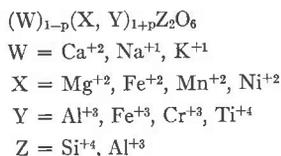
The atomic proportions are calculated on the basis of six oxygen atoms (Table 2). It is assumed that Z positions should be always filled up completely. The result of calculation shows that in most pyroxenes both the Z ions and the sum of the W, X, and Y ions become approximately 2.000, agreeing with the theoretical formula of pyroxenes.

TABLE 1. CHEMICAL COMPOSITIONS OF ORTHOPYROXENES

No.	1	2	3	4	5	6	7
SiO_2	57.63	55.73	55.84	54.11	53.17	53.18	52.83
Al_2O_3	1.20	0.93	1.60	1.52	0.45	3.08	2.42
TiO_2	tr.	tr.	0.19	0.19	0.22	0.21	0.29
Fe_2O_3	0.32	0.65	none	none	1.32	0.25	1.53
FeO	3.20	9.30	9.92	15.73	17.18	18.05	18.05
MnO	0.02	0.15	0.15	0.34	0.48	0.41	0.36
MgO	36.07	31.22	30.96	27.03	23.81	23.26	23.05
CaO	0.89	1.80	1.36	1.16	2.67	2.09	1.45
Na_2O	n.d.	0.21	n.d.	n.d.	0.47	n.d.	n.d.
K_2O	n.d.	tr.	n.d.	n.d.	0.00	n.d.	n.d.
H_2O+	n.d.⎱	0.32	n.d.	n.d.	n.d.	n.d.	n.d.
H_2O-	n.d.⎰		n.d.	n.d.	0.21	0.20	n.d.
P_2O_5	none	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	99.33	100.23	100.02	100.08	99.98	100.73	99.98
Analysts	K. Tada and M. Huzimoto	Y. Kawano and K. Endo	K. Tada and M. Huzimoto	K. Tada and M. Huzimoto	K. Nagashima	T. Kusida	K. Tada and M. Huzimoto

Note: Analysis No. 5 is corrected for 0.5% hematite and recalculated to 100%.

TABLE 1.—*Continued*

No.	8	9	10	11	12	13	14
SiO_2	53.24	53.24	53.32	53.51	53.20	52.07	52.22
Al_2O_3	1.38	1.86	0.88	0.40	1.15	1.70	0.43
TiO_2	0.23	0.38	0.05	0.06	0.13	0.47	0.08
Fe_2O_3	1.05	1.23	0.71	1.50	none	none	0.70
FeO	18.70	19.21	19.91	19.57	21.64	22.65	25.91
MnO	0.85	0.87	1.22	1.05	0.78	0.48	0.83
MgO	23.34	22.18	23.26	23.12	22.50	21.13	18.54
CaO	1.23	0.61	0.74	0.86	0.82	1.55	1.28
Na_2O	tr.	0.35	n.d.	n.d.	n.d.	n.d.	n.d.
K_2O	tr.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.
H_2O+	0.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
H_2O-		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
P_2O_5	tr.	none	n.d.	n.d.	n.d.	n.d.	tr.
Total	100.12	100.00	100.09	100.07	100.22	100.05	99.99
Analysts	S. Tanaka	G. Kozima and S. Taneda	K. Tada and M. Huzimoto	K. Tada and M. Huzimoto	K. Tada and M. Huzimoto	K. Tada and M. Huzimoto	Y. Konisi

Note: Analysis No. 9 is corrected for 0.8% magnetite and 0.55% apatite, and No. 14 for 0.3% ilmenite, and both recalculated to 100%.

TABLE 1—*Continued*

No.	15	18	19	22	23
SiO_2	50.26	49.43	50.04	45.95	46.56
Al_2O_3	3.13	0.38	1.47	0.90	0.23
TiO_2	0.16	0.17	0.00	0.10	0.03
Fe_2O_3	0.65	0.04	0.08	0.31	0.20
FeO	26.54	34.91	30.07	41.65	48.10
MnO	0.76	1.19	4.88	5.02	0.15
MgO	16.36	12.96	12.54	3.49	3.70
CaO	1.76	0.71	0.63	1.43	0.77
Na_2O	0.24	0.02	0.10	n.d.	0.04
K_2O	0.13			n.d.	
H_2O+	n.d.	n.d.	n.d.	0.65	n.d.
H_2O-	n.d.	n.d.	0.02	0.09	n.d.
P_2O_5	n.d.	n.d.	tr.	n.d.	n.d.
Total	99.99	99.81	99.83	99.59	99.78
Analysts	K. Nagashima	Y. Konisi	Y. Konisi	N. F. M. Henry	Y. Konisi

Note: Analysis No. 15 is corrected for 0.5% hematite, 0.8% ilmenite, and 1.0% apatite and is recalculated to 100%.

TABLE 2. ATOMIC PROPORTIONS OF ORTHOPYROXENES CALCULATED ON THE
BASIS OF 6 OXYGEN ATOMS

No.	1		2		3		4	
Si	1.970	2.000	1.960	1.998	1.955	2.000	1.948	2.000
Al	0.030		0.038		0.045		0.052	
Al	0.019		0.000		0.022		0.013	
Ti	0.000		0.000		0.006		0.006	
Fe^{+3}	0.008		0.017		0.000		0.000	
Fe^{+2}	0.090		0.272		0.290		0.471	
Mn	0.000	2.009	0.004	2.022	0.004	1.997	0.011	2.006
Mg	1.849		1.648		1.625		1.460	
Ca	0.033		0.068		0.050		0.045	
Na	0.000		0.013		0.000		0.000	
K	0.000		0.000		0.000		0.000	

No.	5		6		7		8	
Si	1.958	1.980	1.931	2.000	1.938	2.000	1.960	2.000
Al	0.022		0.069		0.062		0.040	
Al	0.000		0.062		0.044		0.022	
Ti	0.007		0.006		0.009		0.007	
Fe^{+3}	0.035		0.009		0.040		0.031	
Fe^{+2}	0.528		0.547		0.552		0.575	
Mn	0.015	2.035	0.013	1.989	0.011	1.980	0.027	2.002
Mg	1.315		1.269		1.267		1.291	
Ca	0.104		0.083		0.057		0.049	
Na	0.031		0.000		0.000		0.000	
K	0.000		0.000		0.000		0.000	

No.	9		10		11		12	
Si	1.960	2.000	1.974	2.000	1.980	1.998	1.969	2.000
Al	0.040		0.026		0.018		0.031	
Al	0.044		0.014		0.000		0.022	
Ti	0.011		0.002		0.002		0.004	
Fe^{+3}	0.035		0.018		0.040		0.000	
Fe^{+2}	0.590		0.613		0.604		0.668	
Mn	0.027	1.989	0.038	2.006	0.033	1.995	0.024	1.999
Mg	1.227		1.292		1.283		1.250	
Ca	0.024		0.029		0.033		0.031	
Na	0.027		0.000		0.000		0.000	
K	0.004		0.000		0.000		0.000	

TABLE 2—*Continued*

No.	13		14		15		18	
Si	1.944	}2.000	1.992	}2.000	1.927	}2.000	1.969	}1.988
Al	0.056		0.008		0.073		0.019	
Al	0.020		0.010		0.065		0.000	
Ti	0.013		0.002		0.005		0.005	
Fe^{+3}	0.000		0.018		0.018		0.000	
Fe^{+2}	0.706		0.824		0.849		1.159	
Mn	0.016	}2.001	0.027	}1.997	0.025	}1.997	0.040	}2.009
Mg	1.183		1.063		0.941		0.774	
Ca	0.063		0.053		0.071		0.031	
Na	0.000		0.000		0.018		0.000	
K	0.000		0.000		0.005		0.000	

No.	19		22		23	
Si	1.976	}2.000	1.976	}2.000	1.987	}1.997
Al	0.024		0.024		0.010	
Al	0.047		0.022		0.000	
Ti	0.000		0.003		0.001	
Fe^{+3}	0.005		0.010		0.005	
Fe^{+2}	0.995		1.491		1.710	
Mn	0.166	}1.993	0.183	}2.000	0.005	}1.996
Mg	0.744		0.224		0.238	
Ca	0.026		0.067		0.035	
Na	0.010		0.000		0.002	
K	0.000		0.000		0.000	

Ca content. As seen from Table 2, the atomic proportion of Ca ranges from 0.104 to 0.057 in Nos. 2, 5, 6, 7, 13, and 15, from 0.053 to 0.045 in Nos. 3, 4, 8 and 14, and from 0.033 to 0.024 in Nos. 9, 10, and 11. The Ca content can be correlated with the temperature of crystallization of the pyroxenes. Thus the pyroxenes Nos. 5, 6, 7, and 13 crystallized in pyroxene andesite (some basaltic andesite) magmas of high temperatures (the pigeonitic rock series of Kuno, 1950); Nos. 3, 4, and 14 in pyroxene andesite and dacite magmas of slightly lower temperatures (the hypersthenic rock series of Kuno, 1950); Nos. 2, 8, and 15 also in pyroxene andesite and dacite magmas but the temperature relations of the magmas are not certain; and Nos. 9, 10, and 11 all in hornblende andesite and dacite magmas of still lower temperatures (the hypersthenic rock series).

The pyroxene No. 5 crystallized during or immediately before the

TABLE 3. MODE OF OCCURRENCE OF ORTHOPYROXENES AND REFERENCES

No.	Mode of occurrence	Reference
1	Main constituent of harzburgite. Few exsolution lamellae.	Kuno, 1941
2	In beach sand. Originally phenocrysts in bronzite andesite.	Kozu and Kawano, 1931
3	Phenocrysts in bronzite andesite.	Kuno, 1947b
4	Phenocrysts in bronzite andesite.	Kuno, 1947b
5	Microphenocrysts in hypersthene-olivine andesite.	Kuno and Naga-shima, 1952
6	Phenocrysts in augite-hypersthene andesite.	Ota, 1952
7	Phenocrysts in augite and olivine-bearing hypersthene andesite.	Kuno, 1941
8	Phenocrysts in hypersthene-augite dacite (pumice).	Kuno, 1938
9	Phenocrysts in hypersthene-hornblende dacite (pumice).	Taneda, 1946
10	Phenocrysts in hypersthene-hornblende-quartz dacite (tuff).	Kuno, 1941
11	Phenocrysts in augite-hypersthene-hornblende andesite (tuff).	Kuno, 1941
12	In hypersthene-cummingtonite-hornblende amphibolite. No exsolution lamellae.	Kuno, 1947a
13	Phenocrysts in augite-pigeonite-hypersthene andesite.	Kuno, 1950
14	Phenocrysts in augite-bearing hypersthene dacite.	Unpublished analysis
15	Phenocrysts in augite-bearing hypersthene dacite (obsidian).	Unpublished analysis
16	Phenocrysts in garnet-bearing ferrohypersthene dacite.	No analysis
17	Phenocrysts in ferrohortonolite-ferrohypersthene dacite (obsidian).	No analysis
18	In ferrohypersthene-hornblende gabbro. A little exsolution lamellae.	Unpublished analysis
19	In eulysite or iron-rich hornfels. No lamellae.	Unpublished analysis
20	Phenocrysts in biotite-ferrohypersthene rhyolite (pitchstone).	No analysis
21	Phenocrysts in subcalcic ferroaugite-eulite-fayalite dacite (pitchstone).	No analysis
22	In eulysite or iron-rich hornfels.	Tsuru and Henry, 1937
23	In eulysite or iron-rich hornfels. A little exsolution lamellae. Parting parallel to 100 and 010.	Unpublished analysis

extrusion of the lava. The exceptionally high proportion of Ca in this pyroxene is discussed elsewhere (Kuno and Nagashima, 1952).

The proportion of Ca in the pyroxenes of the pigeonitic rock series agrees with that in orthopyroxenes crystallized from normal basaltic magmas such as those of Stillwater and Bushveld complexes ($CaO = 1.65$

±0.3%, Hess, 1952). Probably this proportion is normal to the pyroxenes of the pristine basaltic magma whose temperature of crystallization is from 1200° C. to 1000° C. The temperature of basaltic lava of the pigeonitic rock series in Osima volcano, Japan, lies between 1200° C. and 1100° C. (Minakami, 1951). As has been discussed elsewhere (Kuno, 1950), the temperature of crystallization of contaminated magma (the hypersthenic rock series) is lower than that of the pristine basaltic magma.

The proportion of Ca in the pyroxenes from the hornblende-bearing lavas is nearly equal to that in the pyroxenes formed by contact-metamorphism of granitic intrusions (Nos. 12, 19, and 23, Ca = 0.035—0.026) and also to that of the pyroxenes from low-temperature plutonic rocks (Nos. 1 and 18, Ca = 0.033—0.031). In the metamorphic rocks, the orthopyroxenes are associated with cummingtonite, grünerite, and green hornblende. These rocks belong to amphibolite facies. The proportion of Ca in No. 22 is exceptionally high, although the mineral was collected at the same locality as that of No. 19.

The pyroxene No. 1 occurs in serpentinized peridotite which was prob-

TABLE 4. LOCALITIES OF ORTHOPYROXENES

No.	Localities
1	Kamogawa, Tiba Pref.
2	Titi-zima, Bonin Islands.
3	Tyosi, Tiba Pref.
4	Kokubudai, Kagawa Pref.
5	Tengu-zawa, near Hatazyuku, Hakone volcano, Kanagawa Pref.
6	Akagi volcano, Gunma Pref.
7	Tono-mine, near Yumoto, Hakone volcano, Kanagawa Pref.
8	Odawara, eastern foot of Hakone volcano, Kanagawa Pref.
9	Ikaho, Haruna volcano, Gunma Pref.
10	Near Kentyo-zi, Kamakura, Kanagawa Pref.
11	Sitisei-zan, near Tai-pei, north Formosa.
12	Hokizawa, Tanzawa Mountainland, Kanagawa Pref.
13	Hakone-toge, Hakone volcano, Kanagawa Pref.
14	Hirogawara, near Yugawara, Kanagawa Pref.
15	Kaziya, southeastern foot of Hakone volcano, Kanagawa Pref.
16	Northeast of Taguti, Sidara Basin, Aiti Pref.
17	Yosimura, southwestern margin of Sidara Basin, Aiti Pref.
18	Kasimine, near Nizyo-san, southeast of Osaka.
19	Yu-hsi-kou, An-tung-shen, south Manchuria.
20	Kaore, east of Ebi, Sidara Basin, Aiti Pref.
21	Matuki, north of Asio, Totigi Pref.
22	Yu-hsi-kou, An-tung-shen, south Manchuria.
23	Wang-chang-tzu, Je-ho-shen, southwest Manchuria.

ably formed at a temperature lower than that of the ordinary basaltic magma (Hess, 1938). The pyroxene No. 18 occurs in hornblende gabbro closely associated with syn-orogenic granite and is quite different in its petrographic character and mode of occurrence from the normal gabbro.

Probably the orthopyroxenes of these hornblende-bearing igneous and metamorphic rocks and the serpentinized peridotite were formed at temperatures between 900° C. and 600° C.

Hess (1941) postulated that Ca is more soluble in orthopyroxenes at higher temperatures than at lower temperatures. Atlas (1952) demonstrated the relation by his synthetic experiments on the system $MgSiO_3$ —$CaMgSi_2O_6$. It is evident that the larger Ca ion can substitute for smaller Mg ion only at high temperatures and the limit of this substitution narrows as the temperature falls.

According to Atlas' diagram, atomic proportion of Ca in enstatite solid solution is 0.115 at 1100° C., which is the maximum limit of solubility in orthopyroxene, 0.050 at 1000° C., and 0.030 at 700° C. These figures agree very closely with the Ca proportion in the natural orthopyroxenes and the inferred temperature of their formation. We may safely conclude that Ca content in orthopyroxenes can be used as a geothermometer.

Al and Mn content. The proportion of Al varies with that of Ca although there are some exceptions. Thus Al is high in the pyroxenes Nos. 6, 7, 13, and 15, whereas it is low in Nos. 10, 11, 14, 18, and 23. In No. 5 Al is low in spite of high Ca.

Mn content is higher in the pyroxenes from hornblende-bearing igneous rocks (Nos. 9, 10, 11, and 18) than in those from the other igneous rocks. It is markedly high in the two pyroxenes (Nos. 19 and 22) from Yu-hsi-kou mine which were formed from sedimentary rocks rich in Fe and Mn. The associated magnetite deposit is also rich in Mn and was used as manganiferous iron ore.

Optical Properties

The optical properties are listed in Table 5, together with the atomic ratios $Mg:Fe^{+2}+Fe^{+3}+Mn$ calculated from the analyses. In Fig. 1 $N_x N_z N_z - N_x$, and 2V are plotted against these ratios and the curves showing the variation of the optical constants are drawn. The pyroxenes Nos. 3, 4, 19, and 22 are not used for drawing the curves, because the former two show strong zoning and the latter two are unusually rich in Mn.

The change of the type of dispersion of 2V is also shown in the figure. The true change takes place twice throughout the series (Kuno, 1941), but as the dispersion is written in reference to the acute bisectrix in Table

TABLE 5. OPTICAL PROPERTIES OF ORTHOPYROXENES

No.	1	2	3	4	5	6	7	8
$Mg:Fe^{+2}+Fe^{+3}$ +Mn	94:6	85:15	85:15	75:25	69:31	69:31	68:32	67:33
N_x (mean)	1.660	1.672	1.6755	1.6855	1.691	n.d.	1.696	1.691
N_y (mean)	1.664	1.6765	1.6815	1.6935	1.699	n.d.	1.703	1.701
N_z (mean)	1.669	1.681	1.6865	1.6975	1.703	1.7065	1.708	1.705
Range of N_z	±0.000	±0.005	±0.0095	±0.0215	±0.004	±0.0045	±0.005	±0.005
N_z-N_x	0.009	0.009	0.011	0.011	0.012	n.d.	0.012	0.014
2V (mean)	(+)68°	n.d.	(−)80°	(−)82°.5	(−)63°	n.d.	(−)62°	(−)60°.5
Range of 2V	±0°	n.d.	±13°	±9°.5	±1°	n.d.	±4°	±3°.5
Dispersion	$r>v$	None	$r<v$	$r<v, r>v$	$r>v$	n.d.	$r>v$	$r>v$
$\{N_z$ and corre- $\{$sponding 2V	1.669 (+)68°	1.683 (−)84°	n.d. n.d.	n.d. n.d.	1.703 (−)64°	n.d. n.d.	1.708 (−)62°	1.704 (−)61°
Pleochroism	None	None	None	None to weak	Moderate	n.d.	Strong	Moderate

No.	9*	10	11	12	13	14	15	16
$Mg:Fe^{+2}+Fe^{+3}$ +Mn	66:34	66:34	65:35	64:36	62:38	55:45	51:49	?
N_x (mean)	1.6915	1.6955	1.6945	1.693	1.7015	n.d.	n.d.	n.d.
N_y (mean)	1.7005	1.7045	1.7035	1.704	1.7115	n.d.	n.d.	n.d.
N_z (mean)	1.7055	1.7075	1.7075	1.709	1.7145	1.721	1.726	1.735
Range of N_z	±0.0045	±0.0025	±0.0025	±0.001	±0.0025	±0.003	±0.004	±0.006
N_z-N_x	0.014	0.012	0.013	0.016	0.013	n.d.	n.d.	n.d.
2V (mean)	(−)60°.5	(−)63°.5	(−)60°	(−)58°	(−)59°.5	(−)54°.5	(−)52°	(−)54°
Range of 2V	±5°.5	±2°.5	±1°	+1°	±2°.5	±1°	±1°	±1°
Dispersion	$r>v$	$r>v$	$r>v$	$r>v$	$r>v$	$r>v$	None	$r<v$
$\{N_z$ and corre- $\{$sponding 2V	1.706 (−)62°	1.7075 (−)63°.5	1.706 (−)61°	1.706 (−)58°	1.716 (−)57°.5	1.721 (−)54°.5	1.726 (−)52°	1.737 (−)55°
Pleochroism	Moderate	Moderate	Moderate	Moderate	Strong	Moderate	Weak	Weak

* Optical data except for "N_z and corresponding 2V" by Taneda (1946).

No.	17	18	19	20	21	22*	23
$Mg:Fe^{+2}+Fe^{+3}+Mn$	?	39:61	39:61	?	?	12:88	12:88
N_x (mean)	n.d.	n.d.	n.d.	n.d.	n.d.	1.755	1.7545
N_y (mean)	n.d.	n.d.	n.d.	n.d.	n.d.	1.763	1.7645
N_z (mean)	1.7355	1.7385	1.7345	n.d.	1.7705	1.773	1.7745
Range of N_z	±0.0085	±0.0025	±0.0025	n.d.	±0.0035	±0.000?	±0.0025
N_z-N_x	n.d.	n.d.	n.d.	n.d.	n.d.	0.018	0.020†
2V (mean)	(−)58°	(−)53°	(−)54°.5	(−)65°	(+)89°.5	(+)83°	(+)84°
Range of 2V	±2°	±1°	±0°.5	±3°	±7°.5	±0°?	+1°
Dispersion	$r<v$	$r<v$	$r<v$	$r<v$	$r<v, r>v$	$r>v$	$r>v$
N_z and corresponding 2V	1.741 (−)58°	1.7385 (−)53°	1.7345 (−)54°.5	1.751 (−)68°	1.768 (−)83°.5	1.773 (+)83°	1.7745 (+)84°
Pleochroism	Weak	Weak	None	Weak	Strong	Weak?	Moderate

* Optical data by Tsuru and Henry (1937).
† Determined by Hess.
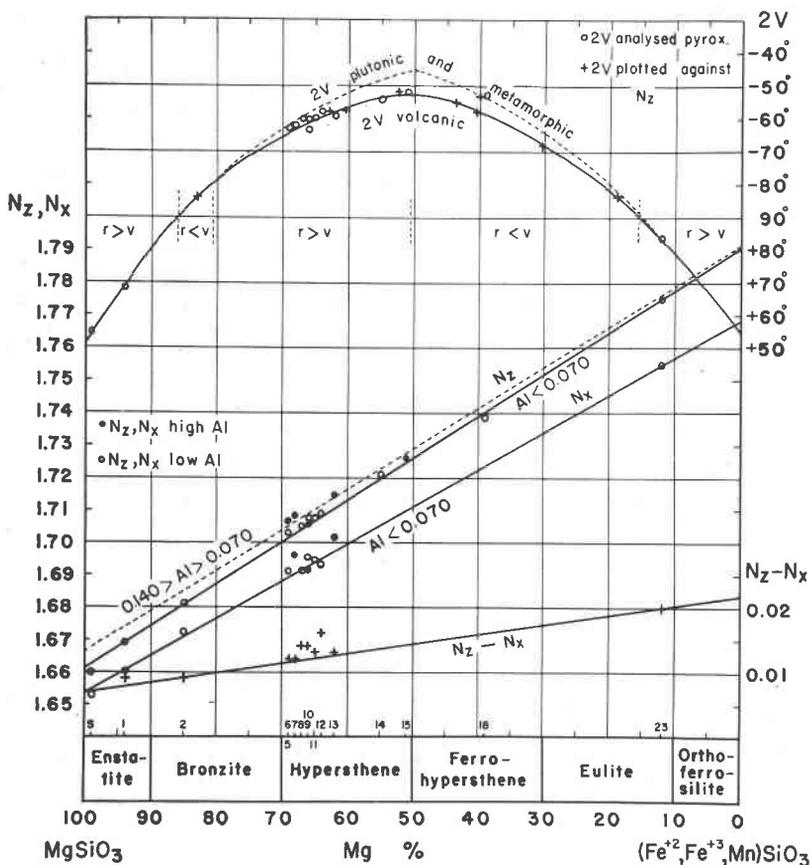
FIG. 1. Variation of optical properties of orthopyroxenes. The numbers in the lower part of the diagram refer to those in Table 1. S—enstatite from Shallowater meteorite.

5, it is shown in the figure as changing also at two points where the 2V curve passes 90°.

Refractive indices. The ranges of the refractive indices were determined on the powders used for the analyses. All the pyroxenes except No. 1 show considerable range of N_z. The error in each determination for the moderately zoned crystals is ± 0.001.

In Fig. 1, points for N_x and N_z of the pyroxenes containing less than 0.070 atomic proportion of Al (both in Si and Mg positions) are shown by open circles. They lie on or very close to a straight line (full lines in Fig. 1). The points for enstatite from Shallowater meteorite (Foshag, 1940) which contains no Al lie a little below the lines. Points for N_x and N_z of the pyroxenes containing 0.140—0.070 Al (solid circles) lie above

the full lines. A dotted line is drawn to show the N_z variation for these aluminous pyroxenes.

Hess (1952) has also drawn the N_z variation curve for the orthopyroxenes of Bushveld type which lies in the middle of the dotted and full lines in Fig. 1. His curve represents N_z variation for orthopyroxenes with medium Al content.

The N_z variation curve given by Poldervaart (1950) nearly coincides with the dotted line.

Mn in orthopyroxenes increases the refractive indices less markedly than Fe^{+2}, as is shown by the lower refractive indices of the manganiferous pyroxene No. 19 than those of No. 18 in spite of their having the same $Mg: Fe^{+2} + Fe^{+3} + Mn$ ratio.

Birefringence. The points for $N_z - N_x$ of the pyroxene No. 23 and the Shallowater enstatite are connected by a straight line. Most of the points for the other pyroxenes lie on or close to this line.

Optic angle. 2V was measured on several crystals of each analyzed pyroxene. The error in each determination for the moderately zoned crystals is $\pm 1°$. The mean values of 2V are plotted in Fig. 1 with open circles.

In order to know the exact variation of 2V of the volcanic orthopyroxenes, several unanalyzed pyroxenes were also studied. N_z and the corresponding value of 2V were measured on one and the same cleavage flake lying on 010 (usually about 0.2 mm. long). The results are given in Table 5. The 2V is plotted against Mg per cent inferred from the corresponding N_z (crosses in Fig. 1).

The points for the volcanic orthopyroxenes lie on a smooth curve (full line in Fig. 1). Hess' (1952) curve for the 2V variation of the orthopyroxenes of Bushveld type (dotted line) lies 7° above the curve for the volcanic pyroxenes at the composition Mg 50, but gradually approaches the latter until the two curves coincide with each other in bronzite and eulite.

Pleochroism. Tables 1 and 5 show that the intensity of pleochroism has no relation to Fe^{+2} or Mn contents. The manganiferous pyroxene No. 19 is colorless. Some relation appears to exist between pleochroism and Ti content.

The strongest pleochroism is seen in the pyroxene No. 13 which has the highest Ti content (0.013). The pleochroism next in intensity is seen in No. 7 which has Ti content (0.009) higher than those of the other pyroxenes except No. 9 (0.011). Nos. 5, 8, 9, 10, 11, 12, 14, and 23 show moderate pleochroism, their Ti contents (except No. 9) varying from 0.007 to 0.001. The colorless pyroxenes (Nos. 1, 2, 3, and 19) have no Ti except No. 3 (0.006).

There may be some exceptions to this rule in the pyroxenes of Bushveld type, because a part of Ti may have been exsolved together with Ca or with Fe^{+2}.

The pleochroism of the two orthopyroxenes are shown below:

Hypersthene No. 13:
X—pale reddish brown
Y—pale greenish brown
Z—pale smoky green
Absorption X>Z>Y

Eulite No. 21:
X—smoky brown
Y—pale brown
Z—smoky green
Absorption Z>X>Y

UNIT CELL DIMENSIONS

Unit cell dimensions a, b, and c were determined by a North American Philips x-ray spectrometer, using Fe K_{α_1} radiation. The method was described by Hess (1952) in detail and will not be repeated here. However, instead of using a bakelite slide as described by Hess, the writer used mixture of the powder of the pyroxenes and that of silicon mounted on a glass slide with Duco cement. The correction for the instrument, the thickness of the layer of the sample, and the roughness of its surface was made by reading the known 2θ angles of the reflections from silicon. For the pyroxenes Nos. 16 and 21, the bakelite slides were used. For Nos. 5 and 14, determinations were made on the two different types of slides; the results agreed within 0.001 Å.

The a and b dimensions were determined by the reflections (14, 5, 0), (060), (12, 0, 0), and (650). The average values of these determinations are given in Table 6. The figures include errors usually less than 0.003 Å and rarely ±0.005 Å. The values are further checked by the reflections (610) and (420).

TABLE 6. UNIT CELL DIMENSIONS (IN Å) OF ORTHOPYROXENES

No.	2	5	6	7	8	10
a(observed)	18.281	18.333	18.320	18.326	18.314	18.309
a(calculated)	18.282	18.325	18.321	18.313	18.307	18.303
b(observed)	8.853	8.885	8.884	8.881	8.884	8.890
c(observed)	5.200	5.218	5.215	5.217	5.214	5.211
c(calculated)	5.205	5.220	5.218	5.216	5.213	5.212
$Mg:Fe^{+2}:Ca$	83:13.5:3.5	67.5:27:5.5	66.5:29:4.5	67.5:29:3.5	67.5:30:2.5	67:31.5:1.5

No.	11	13	14	15	16	21
a(observed)	18.302	18.340	18.337	18.344	18.343	18.429
a(calculated)	18.303	18.323	18.332	18.350	—	—
b(observed)	8.885	8.893	8.920	8.933	8.962	9.016
c(observed)	5.210	5.221	5.220	5.225	5.221	5.249
c(calculated)	5.212	5.219	5.222	5.229	—	—
$Mg:Fe^{+2}:Ca$	67:31.5:1.5	61:36:3	55:42.5:2.5	50.5:45.5:4	45:55*	17:83*

* $Mg:Fe^{+2}+Fe^{+3}+Mn$ estimated from N_z (mean).

The c dimension was obtained by the reflections (004), (502), and (202), using the already known values of a. The average values given in Table 6 include errors less than 0.0004 Å. These values were further checked by the reflections (11, 3, 1) and (131).

In Fig. 2 the observed values of a, b, and c are plotted against Mg: $Fe^{+2}+Fe^{+3}+Mn$ calculated from the analyses or estimated from N_z (mean).
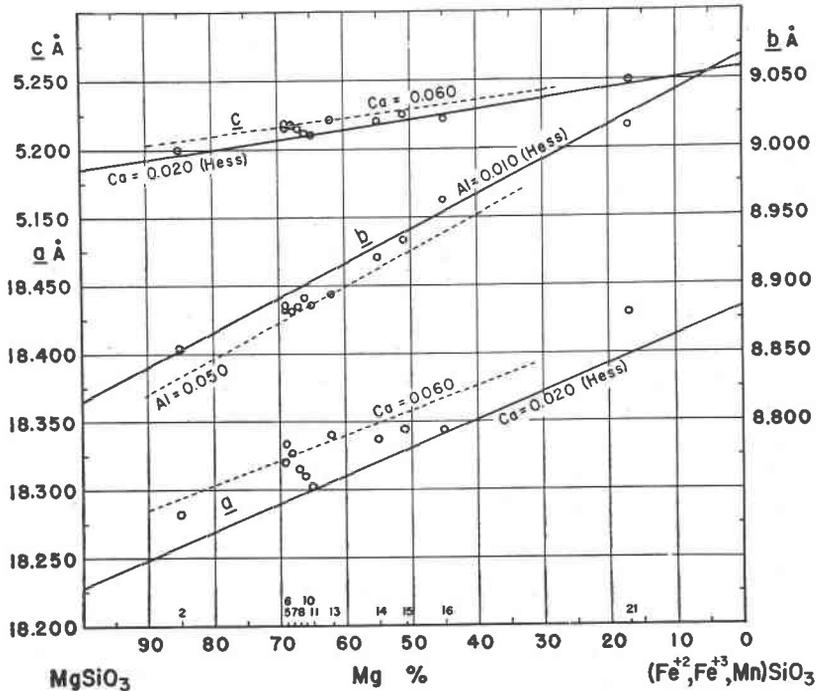
FIG. 2. Variation of unit cell dimensions of orthopyroxenes. The numbers in the lower part of the diagram refer to those in Table 3.

a dimension. The a dimension increases with the amount of Fe^{+2} substituting for Mg but more markedly with the amount of Ca substituting for Mg. This is because Fe^{+2} is larger in ionic radius than Mg, but Ca is larger than Fe^{+2}.

The full line in Fig. 2 is a reproduction of the curve given by Hess (1952) showing the variation of a dimensions of the pyroxenes of Bushveld type including Nos. 18 and 23. The last two pyroxenes contain only 0.031 and 0.035 Ca respectively, yet they show a little exsolution lamellae. Therefore the full line in Fig. 2 represents the a variation for pyroxenes with about 0.020 Ca or with the ratio $Mg+Fe^{+2}:Ca=99:1$.

The points for the volcanic pyroxenes all lie above this line and the amount of departure from this line is proportional to the Ca content of the pyroxenes. Thus the pyroxenes Nos. 10 (Ca=0.029) and 11 (Ca =0.033) lie fairly close to the full line, whereas No. 5 (Ca=0.104) is most removed from the line. A line representing the a variation for pyroxenes with 0.060 Ca or $Mg+Fe^{+2}:Ca=96:4$ is drawn with a dotted line.

The a dimension of any orthopyroxene may be calculated approximately from the following formula:

$$a = \{(O\text{—}Mg) \times l + (O\text{—}Fe^{+2}) \times m + (O\text{—}Ca) \times n - (O\text{—}Mg) \times 100\}$$
$$\times 0.0396 + 18.228 \text{ Å}$$

where l, m, and n are atomic per cent of Mg, Fe^{+2}, and Ca of the given pyroxene respectively, $(O\text{—}Mg)$, $(O\text{—}Fe^{+2})$, and $(O\text{—}Ca)$ are the interatomic distances between oxygen and Mg, Fe^{+2}, and Ca ions respectively, and 18.228 Å is the a dimension of enstatite $(Mg:Fe^{+2}:Ca=99:0:1)$ obtained from the full line in Fig. 2. The interatomic distances used here are as follows: $(O\text{—}Mg)=2.1$ Å, $(O\text{—}Fe^{+2})=2.15$ Å, $(O\text{—}Ca)=2.3$ Å.

The atomic per cent $Mg:Fe^{+2}:Ca$ of the analyzed pyroxenes and the calculated a for these compositions are shown in Table 6. The calculated values agree fairly closely with the observed values.

b dimensions. The b dimension increases with the amount of Fe^{+2} but decreases with the amount of Al substituting for Mg, because Fe^{+2} is larger than Mg but Al is smaller than Mg.

In Fig. 2 is reproduced the line given by Hess (1952) showing the b variation for orthopyroxenes with about 0.010 Al in Mg position, including the pyroxenes Nos. 18 and 23.

Most of the volcanic pyroxenes contain larger amounts of Al in Mg position, so that the points lie generally below the line. A dotted line is drawn to show the b variation for pyroxenes containing 0.050 Al in Mg position.

c dimension. This also increases with the amounts of Fe^{+2} and Ca substituting for Mg, but the rate of increase is smaller than that in a dimension. The full line in Fig. 2 shows the c variation for pyroxenes with 0.020 Ca, whereas the dotted line for those with 0.060 Ca.

The c dimension of the analyzed pyroxenes can be calculated from the following formula:

$$c = \{(O\text{—}Mg) \times l + (O\text{—}Fe^{+2}) \times m + (O\text{—}Ca) \times n - (O\text{—}Mg) \times 100\}$$
$$\times 0.0142 + 5.185 \text{ Å}.$$

The result of calculation (Table 6) shows a close agreement with the observed values.

Discussion of the Result

The present study indicates that the refractive indices and unit cell dimensions of the volcanic orthopyroxenes vary with the chemical compositions entirely in the same way as found in the orthopyroxenes of the Bushveld type. These physical constants show straight line variations if they are plotted against the atomic ratio $Mg: Fe^{+2} + Fe^{+3} + Mn$, provided the proportion of Ca and Al is constant.

The effects of Fe^{+2}, Ca, and Al on the unit cell dimensions can be explained as due to the difference of their ionic radii from that of Mg for which they substitute.

The only difference between the volcanic orthopyroxenes and those of Bushveld type is found in the variation of 2V according to Mg per cent. Even this might be a result of the difference of Ca content between the two groups (Hess, 1952). It is also possible that the order-disorder relation in the orthopyroxene structure causes this difference. In order to decide whether this difference is related to Ca content, it is necessary to study volcanic orthopyroxenes about Mg50 but with low Ca content.

We can determine Mg per cent of orthopyroxenes by measuring N_z. Then by measuring the a and b dimensions, we can find Ca and Al content of that crystal.

It will be interesting to determine Ca content of orthopyroxenes crystallized in recent lavas whose temperatures are actually measured.

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