

CELL PARAMETERS OF ORTHOPYROXENES

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ABSTRACT

The cell parameters have been determined for forty-seven analyzed orthopyroxenes from metamorphic rocks, the majority of them from the charnockite series or from related rock types in the granulite facies. In general the cell dimensions are each smaller than those determined by Hess and by Kuno for igneous orthopyroxenes of equivalent compositions. The *a* and *b* dimensions may be considerably less: these are both apparently affected particularly by the amount of Al in the octahedral position and also by the Fe³⁺, Ti, Ca and Mn content of the mineral. The *c* dimension is relatively less affected by these ionic substitutions and may be used to give an approximate value for the Fe²⁺:Mg ratio; the *b* dimension may then be used to give some indication of the alumina content of the orthopyroxene. It is suggested that the departure from linearity of the cell dimensions of various orthopyroxenes reported by Ramberg and De Vore, and taken as evidence of the non-ideal nature of the orthopyroxene mixed crystal series, may be interpreted also in terms of variation in the alumina content (and paragenesis) of the orthopyroxenes studied. Thirteen new orthopyroxene analyses are presented.

INTRODUCTION

The structure and cell parameters of the orthorhombic pyroxene enstatite were investigated by Warren and Modell (1930), and the relationship between the cell parameters and composition of the orthopyroxene series was examined by Ramberg and De Vore (1951). The latter authors concluded both from cell parameters and refractive indices that the orthopyroxenes do not form an ideal mixed-crystal series. Hess (1952) and Kuno (1954), however, have demonstrated straight line relationships between cell parameters and mol. per cent. enstatite in orthopyroxenes from volcanic and plutonic igneous rocks, provided that the proportion of Ca and Al is constant. Clavan *et al.* (1954) investigated orthopyroxenes ranging from 27.8 to 44.3 mol. per cent. FeSiO₃ but, within the limits of error of measurement, found no differences in the spacing between the mineral with the lowest iron content and that with the highest. The present work was undertaken to investigate the variation in cell parameters of orthopyroxenes which had crystallized under granulite facies conditions, and it was soon apparent that the cell dimensions, *a*, *b* and *c*, of these orthopyroxenes were appreciably smaller than for those of equivalent composition but of igneous origin. This investigation has therefore been extended to cover the whole of the common range of Fe²⁺:Mg ratios in the orthopyroxene series and also to include varieties relatively rich in alumina.

CHEMISTRY

New chemical analyses for thirteen orthopyroxenes

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are given in Tables 1 and 2 and previously published analyses for 34 orthopyroxenes investigated in the present study are collected together in Table 3. The analyses were mostly made using the "classical" or mainly gravimetric methods of Washington (1930). The development of the flame photometer, however, has allowed more accurate and reliable determinations of the alkalis in minerals such as these, with a relatively low alkali content, compared with results previously obtainable from the Lawrence Smith method in which the 'blank' values were often considerably in excess of the values being determined. It has thus been possible to re-determine the alkali content of several of the previously analysed orthopyroxenes (Howie, 1955), and the revised values are quoted here. In selecting specimens for this investigation it was desired to select orthopyroxenes of widely varying Fe:Mg ratios and also to study minerals particularly rich in Mn or Al. A fairly wide range of compositions was in fact obtained (Fig. 1) and gaps in the sequence have been obviated by the inclusion of data for seven orthopyroxenes analysed by other investigators. The metal ions, on the basis of six oxygens, have been calculated and are also given in Tables 1 to 3, together with such optical data as are available.

CELL DIMENSION DETERMINATIONS

The measurements of cell dimensions were made over a period of some years, employing in the early stages of the investigation powder cameras of radius 19 cm and later Philips x-ray diffractometers. For the majority of specimens two determinations have been made, and in particular all the early results using a film technique have been re-checked using the

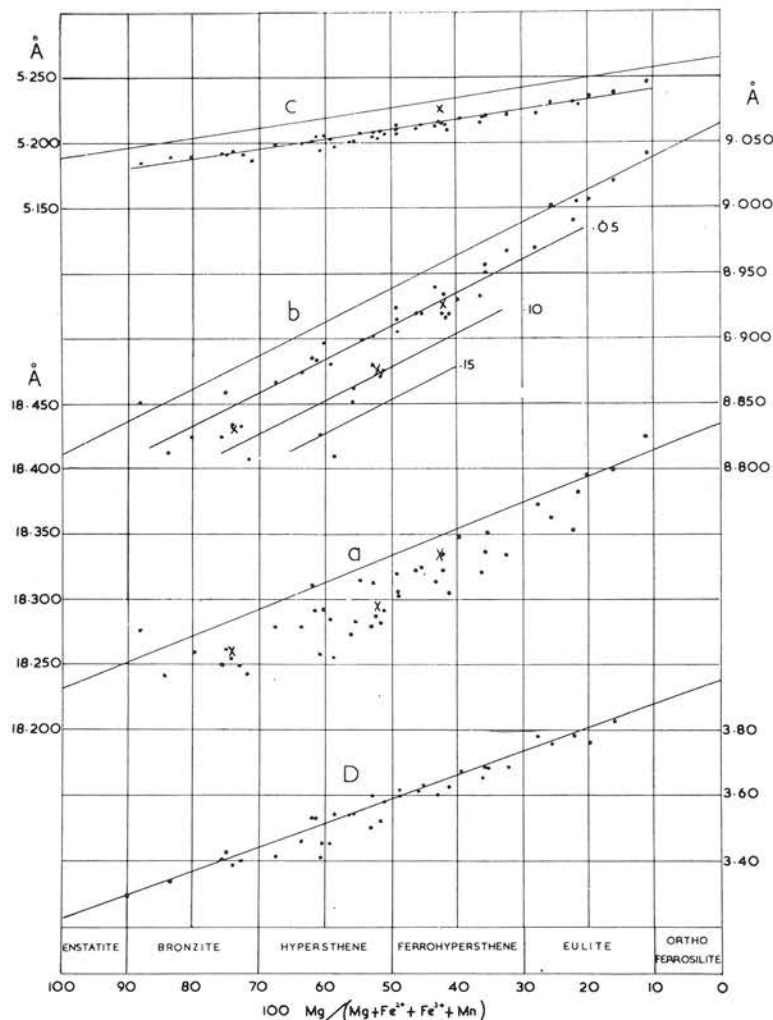


FIG. 1. Variation in cell parameters and specific gravity of orthopyroxenes. For *a*, *b* and *c* the top curve is that of Hess (1952), and for *b* and *c* the lower curves are those plotted to fit the determinations in this paper, as shown by dots; crosses represent values obtained by Hess for three of the author's specimens.

chart recorder. Filtered $FeK\alpha$ or $CoK\alpha$ radiation was used in conjunction with a silicon standard: the error for *b* is estimated to be $\pm 0.006 \text{ \AA}$.

Following Ramberg and De Vore (1951), the *a* and *b* dimensions were measured initially on 12, 0, 0 and 060 and refined by reference to 14, 5, 0, 650, 250 and also 840. The *c* dimension was measured from the 004 reflection.

X-RAY RESULTS

The *a* and *b* dimensions for twelve orthorhombic pyroxenes from the Madras charnockite series were initially determined. The *c* dimensions were not at first measured as little change was expected in the direction of the SiO_3 chains, and because 004, the only reflection of the type 00*l*, was weak. Shortly

after the x-ray work on these twelve minerals had been completed (Howie, 1953), a study on the ion substitutions and changes in unit cell dimensions in orthopyroxenes of the Bushveld type was published (Hess, 1952). It was immediately obvious that there was an apparent discrepancy between the curves drawn for the orthopyroxenes examined by Hess, of which only one was metamorphic, and the results obtained for the charnockitic orthopyroxenes. Professor Hess kindly examined seven of the author's specimens and found general agreement: the average variation in 2θ for 14,5,0 $_{\alpha_1}$ was -0.06° . He also investigated an orthopyroxene (12700 of Table 3) from his own specimen of a Madras charnockite and found that the results gave smaller cell dimensions than indicated by his curves for Bushveld type orthopyroxenes.

It was therefore evident that the Madras charnockitic orthopyroxenes have smaller a and b cell dimensions than those of Bushveld type igneous orthopyroxenes of equivalent Fe/Mg ratio, and that this contraction might be due to the substitution of smaller ions in place of Fe^{2+} or Mg^{2+} . Further investigations were thus made on orthopyroxenes covering a wide range of chemical compositions and from many other areas, though the study was restricted primar-

TABLE 1. NEW ANALYSES, CELL PARAMETERS, ETC. OF ORTHOPYROXENES FROM AMERICA

	A	177/54	KS137/59	B310	400	186b/54	355
SiO_2	51.45	47.11	48.71	48.75	49.54	48.21	48.70
TiO_2	0.08	0.19	0.06	0.10	0.30	0.17	0.10
Al_2O_3	2.52	9.48	4.52	3.90	1.89	1.37	1.04
Fe_2O_3	0.63	2.65	1.63	0.75	0.57	1.46	0.16
FeO	22.60	21.15	26.80	29.05	33.23	36.90	42.35
MnO	0.51	0.30	0.27	0.35	0.73	0.68	0.06
MgO	21.20	19.05	17.04	16.25	12.65	10.45	6.88
CaO	0.65	0.10	0.69	0.58	0.93	0.43	0.85
Na_2O	0.02	tr.	0.04	0.07	0.07	0.00	0.01
K_2O	0.01	0.00	0.08	0.04	0.03	0.00	0.00
H_2O^+	0.05	0.05	—	—	0.05	—	0.02
H_2O^-	0.09	0.17	0.05	0.02	0.22	0.09	0.08
Total	99.81	100.25	99.89	99.86	100.21	99.76	100.25
D	3.53	3.545	3.52(+)	—	3.67	3.68	3.78
$a\text{\AA}$	18.290	18.255	18.282	18.305	18.348	18.334	18.354
$b\text{\AA}$	8.882	8.810	8.871	8.805	8.930	8.967	8.990
$c\text{\AA}$	5.206	5.195	5.208	5.211	5.218	5.222	5.232
Atomic percentages of end-members							
Fe	38.0	41.2	47.7	50.3	59.2	67.0	76.1
Mg	60.7	58.6	50.8	48.5	38.8	32.1	22.0
Ca	1.3	0.2	1.5	1.2	2.0	0.9	1.9
En	61.5	58.7	51.5	49.0	39.6	32.4	22.4
Numbers of metal ions on the basis of 6(O)							
Si	1.927	1.759	1.871	1.888	1.961	1.952	1.999
Al	0.073	.241	.129	.112	.039	.048	.001
Al	0.047	.178	.076	.066	.049	.017	.051
Fe^{3+}	0.018	.075	.046	.022	.017	.045	.005
Mg	1.183	1.060	.975	.938	.746	.631	.421
Ti	0.002	.005	.002	.003	.009	.005	.003
Fe^{2+}	0.708	.660	.861	.941	1.100	1.249	1.454
Mn	0.016	.009	.009	.011	.024	.023	.002
Na	0.001	—	.003	.005	.005	—	.001
Ca	0.026	.004	.028	.024	.039	.018	.038
K	—	—	.004	.002	.001	—	—
ΣY	2.00	1.99	2.00	2.01	1.99	1.99	1.98

Analyst: R. A. Howie.

- A. Hypersthene, enclave of basic rock in granite gneiss, 300 yards W.S.W. of 177/54, S.W. of Dadanawa, South Savannas, British Guiana.
- 177/54. Hypersthene, enclave of basic rock in granite gneiss, 6 miles S.W. of Dadanawa, South Savannas, British Guiana (γ 1.724).
- KS137/59. Hypersthene, pyroxene granulite with charnockitic affinities, northern Quebec, Canada (55°09' N., 68°47' W.).
- B310. Hypersthene, intermediate member of the charnockite series, Bahia, Brazil (Beagle Collection).
400. Ferrohypersthene, charnockite, Panguirtung, east coast of Baffin Island.
- 186b/54. Ferrohypersthene, enderbite, 3 miles W. of Dadanawa, South Savannas, British Guiana.
355. Eulite, garnet-orthopyroxene-quartz rock, 6 miles E.S.E. of Pond Inlet, northeast Baffin Island (γ 1.769).

TABLE 2. NEW ANALYSES, CELL PARAMETERS, ETC. OF ORTHOPYROXENES FROM ELSEWHERE

	20486	SP.18	116	7725	1002	XI-132
SiO_2	53.25	50.39	48.98	48.29	47.55	47.67
TiO_2	0.19	0.20	0.17	0.40	0.07	0.07
Al_2O_3	4.05	2.83	5.76	2.83	1.90	0.43
Fe_2O_3	1.58	1.25	1.04	1.23	0.41	0.95
FeO	11.05	23.84	24.85	33.67	39.37	43.05
MnO	0.09	0.46	0.17	0.67	0.89	0.20
MgO	28.78	20.52	18.50	10.77	8.68	6.24
CaO	0.88	0.58	0.20	2.29	1.23	1.45
Na_2O	0.03	0.04	0.02	0.03	—	0.06
K_2O	0.01	0.01	0.02	0.04	—	0.03
H_2O^+	0.02	0.05	—	0.03	0.05	—
H_2O^-	0.04	tr.	0.13	0.04	0.09	0.03
Total	100.13	100.17	99.84	100.29	100.24	100.18
D	3.36	3.53	3.54	3.68	3.78	3.76
$a\text{\AA}$	18.255	18.288	18.272	18.352	18.374	18.396
$b\text{\AA}$	8.824	8.868	8.850	8.950	8.969	9.102
$c\text{\AA}$	5.192	5.200	5.201	5.221	5.233	5.236
Atomic percentages of end-members						
Fe	19.3	40.5	43.8	61.3	70.1	77.3
Mg	79.0	58.3	55.8	33.6	27.2	19.5
Ca	1.7	1.2	0.4	5.1	2.7	3.2
En	80.3	59.0	56.1	35.5	27.8	20.0
Numbers of metal ions on the basis of 6(O)						
Si	1.888	1.901	1.856	1.921	1.941	1.981
Al	.112	.099	.144	.079	.059	.019
Al	.061	.027	.114	.052	.034	.002
Fe^{3+}	.042	.036	.030	.040	.012	.030
Mg	1.521	1.153	1.045	.642	.531	.386
Ti	.005	.006	.005	.012	.002	.002
Fe^{2+}	.328	.752	.787	1.115	1.338	1.496
Mn	.003	.015	.006	.023	.031	.007
Na	.002	.003	.001	.002	—	.005
Ca	.033	.023	.008	.098	.054	.064
K	.001	.001	.001	.003	—	.001
ΣY	2.00 ¹	2.02	2.00	1.99	2.00	1.99

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20486. Bronzite, pyroxenite ("ultrabasic charnockite"), Dangin, Western Australia (rock analysis and description given by Prider, 1945). (Anal. includes Cr_2O_3 0.08, P_2O_5 0.08).
- SP.18. Hypersthene, norite, Namaqualand, South Africa.
116. Hypersthene, garnetiferous enderbite, Magazine Hill, Madras, India.
7725. Ferrohypersthene, two-pyroxene granulite, Eie, Hitterö, Norway.
1002. Eulite, eulysitic rock, Madial, southern Sudan (α 1.736, β 1.747, γ 1.752; $2V\alpha$ 63°).
- XI-132. Eulite, "ferrohypersthene" with orthopyroxene, grunerite and hastingsite, Okopi valley, Okandja, central Gabon, Africa (rock analysis and description given by Choubert, 1954).

¹ Includes Cr 0.002.

ily to metamorphic orthopyroxenes. Hess (1952) demonstrated that the c dimension also increased with Fe^{2+} and this dimension was determined on the Madras minerals already examined. The results of the cell parameter determinations on forty-seven analysed orthopyroxenes are given in Tables 1 to 3, and the values are plotted in Fig. 1 against molecular percentage En, or more exactly as $100 \text{ Mg}^{2+}/(\text{Mg}^{2+} + \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}^{2+})$, following Hess (*loc. cit.*).

(Text continued on page 219, Col. 2)

TABLE 3. ORTHOPYROXENE ANALYSES, CELL PARAMETERS, ETC.

	1	R.62	H.66	R.104	3709	4645	35	1631	H.67
SiO ₂	55.456	53.63	52.94	54.57	52.10	51.69	50.14	51.76	51.22
TiO ₂	—	0.19	0.09	0.08	0.10	0.15	1.05	0.17	0.13
Al ₂ O ₃	2.026	4.53	4.45	1.53	4.35	4.55	6.02	2.82	2.59
Fe ₂ O ₃	—	1.54	1.27	1.52	1.38	0.55	1.83	1.46	1.87
FeO	8.424	9.07	13.85	14.54	15.28	16.51	15.38	18.30	20.76
MnO	—	0.25	0.26	0.26	0.28	0.27	0.36	0.35	0.62
MgO	34.483	30.31	26.72	27.24	26.65	25.74	24.58	23.21	22.30
CaO	—	0.53	0.35	0.35	0.06	0.50	0.30	1.75	0.57
Na ₂ O	—	0.02	tr.	0.02	0.01	0.03	0.06	0.03	0.03
K ₂ O	—	0.00	0.00	0.00	tr.	0.02	0.05	0.00	0.00
H ₂ O ⁺	—	0.03	n.d.	0.02	0.04	0.04	0.18	n.d.	0.05
H ₂ O ⁻	—	0.04	0.03	0.03	0.05	0.05	0.06	0.03	0.06
Total	100.389	100.14	99.96	100.16	100.30	100.10	100.32	99.88	100.20
Fe	12.0	16.2	24.1	24.5	26.1	27.0	28.2	31.4	36.0
Mg	88.0	82.7	75.2	74.8	73.8	72.0	71.2	65.1	62.9
Ca	—	1.1	0.7	0.7	0.1	1.0	0.6	3.5	1.1
En	88.0	83.6	75.8	75.0	73.9	72.6	71.6	67.5	63.6
<i>Cell parameters and optical properties</i>									
<i>a</i> Å	18.276	18.243	18.250	18.261	18.254	18.248	18.242	18.278	18.278
<i>b</i> Å	8.850	8.812	8.824	8.858	8.833	8.833	8.807	8.865	8.874
<i>c</i> Å	5.184	5.190	5.191	5.191	5.194	5.191	5.186	6.199	5.200
<i>D</i>	—	3.339	3.40	3.429	3.39	3.40	—	3.415	3.46
<i>γ</i>	1.671	—	—	—	1.690	1.690	1.704	—	1.703
2 <i>V</i> _α	94°	—	—	—	73°	76°	76°	62½°	62°
<i>Numbers of metal ions on the basis of 6(O)</i>									
Si	1.924	1.884	1.899	1.962	1.878	1.883	1.822	1.911	1.910
Al	.076	.116	.101	.038	.122	.117	.178	.089	.090
Al	.007	.072	.087	.027	.063	.076	.080	.034	.022
Fe ³⁺	—	.041	.034	.041	.037	.015	.050	.041	.049
Mg	1.783	1.585	1.428	1.457	1.432	1.384	1.331	1.277	1.247
Ti	—	.006	.002	.002	.003	.004	.029	.005	.003
Fe ²⁺	.244	.266	.415	.436	.461	.499	.467	.565	.644
Mn	—	.007	.008	.008	.008	.009	.011	.011	.019
Na	—	.001	—	.001	.001	.002	.004	.002	.001
Ca	—	.020	.014	.014	.002	.019	.012	.069	.022
K	—	—	—	—	—	.001	.002	—	—

1. Bronzite, sagvandite, Sagvandet, 15 km southwest of Lyngen, Troms, Norway (Barth, 1926). Anal. H. Rosenbusch.
- R.62. Bronzite, ultrabasic gneiss, Loch Ossigary, Rodil, South Harris (Howie, 1963).
- H.66. Bronzite, pyroxenite, ½ mile northwest of Scourie House, Scourie, Sutherland (O'Hara, 1961). Anal. R. A. Howie (note: SiO₂ value is 52.94, not 52.44 as quoted in O'Hara, 1961).
- R.104. Bronzite, pegmatitic vein in pyroxene granulite, Caisteal Ard, Ardvourlie, North Harris (Howie, 1963).
3709. Bronzite, ultrabasic rock of the charnockite series,

- Pammal Hill, Pallavasa, Madras (Howie, 1955; alkalis redetermined).
4645. Bronzite, pyroxenite (charnockite series), Pammal, Madras (Howie, 1955).
35. Bronzite, metamorphosed peridotite, Dawros, Connemara, Eire (Rothstein, 1958). Anal. E. A. Vincent (includes Cr₂O₃ 0.26, NiO 0.05; Cr 0.008, Ni 0.001).
1631. Hypersthene, bytownite-orthopyroxene-hornblende-biotite rock, southwest of Lough Fadda, Co. Galway (Leake, 1958). Anal. R. A. Howie.
- H.67. Hypersthene, intermediate charnockitic rock, northwest of Pairc a'Chladaich, Scourie, Sutherland (Howie, 1963).

TABLE 3. ORTHOPYROXENE ANALYSES, CELL PARAMETERS, ETC.—*Cont.*

	R.13b	B.20	2270	4641B	R.96	80258	2941	80270
SiO ₂	51.78	48.48	51.17	50.47	49.68	49.52	49.55	50.21
TiO ₂	0.08	0.52	0.15	0.65	0.11	0.15	0.30	0.12
Al ₂ O ₃	1.96	7.21	1.97	3.55	4.41	2.86	2.42	2.52
Fe ₂ O ₃	1.55	1.97	0.59	0.90	1.68	0.62	1.92	1.93
FeO	21.56	20.62	23.01	23.59	24.21	26.31	26.51	26.10
MnO	0.64	0.49	0.87	0.54	0.48	0.23	0.32	0.70
MgO	21.70	19.97	20.75	20.18	18.32	18.10	17.67	17.80
CaO	0.67	0.46	0.90	0.10	0.76	0.96	0.70	0.66
Na ₂ O	0.01	0.02	0.01	0.04	0.02	tr.	0.02	0.02
K ₂ O	tr.	0.00	tr.	0.02	0.01	0.00	0.02	tr.
H ₂ O ⁺	n.d.	n.d.	n.d.	0.09	0.07	0.70	0.06	0.04
H ₂ O ⁻	0.12	0.07	0.14	0.10	0.05	0.27	0.05	0.02
Total	100.07	99.81	99.56	100.23	99.80	99.72	99.54	100.12
Fe	37.2	38.8	39.1	40.8	43.9	44.7	46.8	46.6
Mg	61.4	60.2	59.1	59.0	54.5	53.3	51.8	52.0
Ca	1.4	1.0	1.8	0.2	1.6	2.0	1.4	1.4
En	62.0	60.8	60.2	59.1	55.5	54.4	52.6	52.6
<i>Cell parameters and optical properties</i>								
<i>a</i> Å	18.311	18.257	19.292	18.283	18.282	18.315	18.278	18.312
<i>b</i> Å	8.884	8.825	8.896	8.879	8.862	8.898	8.878	8.902
<i>c</i> Å	5.202	5.193	5.206	5.203	5.202	5.208	5.205	5.209
D	3.530	3.41	3.54	3.45	3.55	—	3.50	3.60
γ	—	1.719	1.708	1.708	—	1.726	1.722	1.725
2 <i>V</i> _{α}	—	—	58°	58°	—	—	54°	—
<i>Numbers of metal ions on the basis of 6(O)</i>								
Si	1.936	1.811	1.936	1.897	1.886	1.914	1.911	1.920
Al	.064	.189	.064	.103	.114	.086	.089	.080
Al	.022	.128	.024	.057	.084	.044	.021	.034
Fe ³⁺	.045	.056	.017	.025	.048	.018	.056	.056
Mg	1.207	1.112	1.170	1.130	1.037	1.043	1.016	1.015
Ti	.002	.015	.004	.018	.003	.004	.009	.004
Fe ²⁺	.673	.644	.728	.741	.769	.850	.855	.835
Mn	.020	.015	.028	.017	.016	.008	.010	.023
Na	—	.001	.001	.003	.001	—	.001	.001
Ca	.027	.018	.036	.004	.031	.039	.029	.027
K	—	—	—	.001	—	—	.001	—

- R.13b. Hypersthene, hornblende-pyroxene-plagioclase gneiss, north of Rodil, South Harris (Howie, 1963).
- B.20. Hypersthene, hypersthene-spinel-plagioclase hornfels, Belhelvie, Aberdeenshire (Howie, 1963).
2270. Hypersthene, intermediate rock of the charnockite series, Salem, Madras (Howie, 1955; alkalis redetermined).
- 4641B. Hypersthene, intermediate rock of the charnockite series, Shevaroy Hills, Madras (Howie, 1955; alkalis redetermined).
- R.96. Hypersthene, plagioclase—two pyroxene granulite, north of Leverburgh, South Harris (Howie, 1963).
80258. Hypersthene, charnockitic gneiss, Bemato, Betroka, Madagascar (Howie, 1958).
2941. Hypersthene, basic member of charnockite series, Nagaramalai, Salem, Madras (Howie, 1955; alkalis redetermined).
80270. Hypersthene, charnockitic gneiss, Fort Dauphin, Madagascar (Howie, 1958).
- J.32. Hypersthene, charnockitic granulite, Kailasgarh, Vellore, India (Naidu, 1954). Anal. H. Schwander (Includes P₂O₅ 0.05).
- Ch.113. Hypersthene, garnetiferous enderbite, Pallavaram, Madras (Howie and Subramaniam, 1957).

TABLE 3. ORTHOPYROXENE ANALYSES, CELL PARAMETERS, ETC.—Cont.

	J.32	Ch.113	137	7286	3	68671	S.347	12700	4642A
SiO ₂	48.65	50.05	49.44	49.98	47.10	49.73	49.48	49.49	49.50
TiO ₂	1.60	0.30	0.15	0.18	0.20	0.11	0.13	0.14	0.11
Al ₂ O ₃	1.66	4.08	2.21	2.26	3.25	1.96	1.77	1.78	2.01
Fe ₂ O ₃	5.55	0.68	1.93	1.05	1.74	1.72	1.84	0.54	1.31
FeO	24.40	27.50	28.06	27.97	29.03	29.64	31.56	32.48	32.60
MnO	0.30	0.27	1.03	0.60	0.64	0.53	0.49	0.66	0.59
MgO	17.65	16.51	16.61	15.82	14.76	14.66	14.25	13.73	13.74
CaO	0.12	0.46	0.23	1.81	3.43	1.24	0.80	1.16	0.16
Na ₂ O	0.27	0.09	0.10	0.11	tr.	0.10	0.01	0.00	0.03
K ₂ O	tr.	0.03	tr.	0.07	0.00	0.01	tr.	0.00	0.02
H ₂ O ⁺	0.03	0.02	0.04	n.d.	n.d.	0.04	0.02	0.04	0.01
H ₂ O ⁻	0.01	0.11	0.29	0.21	—	0.11	0.04	0.09	0.02
Total	100.29	100.10	100.09	100.06	100.15	99.85	100.39	100.11	100.10
Fe	48.5	48.5	50.5	49.1	50.4	53.3	55.8	56.3	58.2
Mg	51.3	50.5	49.0	47.1	42.5	44.1	42.5	41.3	41.5
Ca	0.2	1.0	0.5	3.8	7.1	2.6	1.7	2.4	0.3
En	51.4	51.0	49.2	49.0	45.7	45.3	43.2	42.4	41.6
<i>Cell parameters and optical properties</i>									
<i>a</i> Å	18.286	18.291	18.320	18.302	18.323	18.325	18.314	18.334	18.322
<i>b</i> Å	8.875	8.876	8.923	8.915	8.919	8.918	8.939	8.919	8.933
<i>c</i> Å	5.204	5.207	5.213	5.207	5.212	5.216	5.214	5.216	5.215
D	3.33	3.58	3.60	3.61	3.60±	3.63	3.60	3.65	—
γ	1.724	1.728	1.724	1.725	1.735	1.732	1.733	1.737	1.735
2V _α	54°	—	52°	—	57°	52°	54°	54.5°	56°
<i>Numbers of metal ions on the basis of 6(O)</i>									
Si	1.868	1.918	1.917	1.937	1.851	1.945	1.940	1.949	1.946
Al	.075	.082	.083	.063	.149	.055	.060	.051	.054
Al	—	.102	.019	.041	.001	.034	.020	.034	.039
Fe ³⁺	.106	.019	.056	.031	.051	.052	.054	.014	.039
Mg	1.010	.943	.965	.915	.864	.854	.837	.810	.805
Ti	.046	.009	.005	.005	.006	.002	.004	.005	.003
Fe ²⁺	.784	.879	.907	.903	.954	.968	1.030	1.065	1.072
Mn	.010	.009	.034	.019	.021	.018	.016	.021	.020
Na	.020	.009	.009	.008	—	.009	.001	—	.002
Ca	.005	.018	.009	.075	.144	.051	.034	.047	.007
K	—	.001	—	.003	—	—	—	—	.001

137. Ferrohpersthene, intermediate member of the charnockite series, Ambagamudam Pothai, Tinnevely, Madras (Howie, 1955).
7286. Ferrohpersthene, basic member of the charnockite series, Lafit Mountains, Sudan (Howie, 1958).
3. Ferrohpersthene, basic charnockitic granulite, near Lafler Canyon, Santa Lucia range, California (Compton, 1960).
68671. Ferrohpersthene, intermediate member of the charnockite series, Hatton, Ceylon (Howie and Subramaniam, 1957).
- S.347. Ferrohpersthene, intermediate member of the charnockite series, Mt. Wati, West Nile district, Uganda (Howie and Subramaniam, 1957).
12700. Ferrohpersthene, charnockite, Pallavaram, Madras (Howie, 1955). Anal. Rock Anal. Lab., Univ. of Minnesota.
- 4642A. Ferrohpersthene, basic member of the charnockite series, Pallavaram, Madras (Howie, 1955, alkalis re-determined).
- Ch.199. Ferrohpersthene, basic member of the charnockite series, Pallavaram, Madras (Howie and Subramaniam, 1957).
4639. Ferrohpersthene, charnockite, Pallavaram, Madras (Howie, 1955).
6436. Ferrohpersthene, charnockite, Trisul Hill, Meanambakam, Madras (new analysis).
115. Ferrohpersthene, intermediate member of the charnock-

TABLE 3. ORTHOPYROXENE ANALYSES, CELL PARAMETERS, ETC.—*Cont.*

	Ch.199	4639	6436	115	V.2	H.4	UG.29a	A.50
SiO ₂	49.28	47.98	47.11	47.23	47.33	47.8	46.65	47.1
TiO ₂	0.17	0.94	0.29	1.02	0.29	—	0.10	—
Al ₂ O ₃	2.09	3.39	2.79	2.47	1.37	0.2	2.10	0.2
Fe ₂ O ₃	0.98	1.54	1.98	1.60	1.09	2.3	0.57	4.1
FeO	32.01	32.16	33.72	34.03	39.41	40.4	44.02	40.1
MnO	0.47	0.26	0.28	0.89	0.94	0.52	0.55	3.1
MgO	13.32	13.16	13.34	11.14	8.02	6.67	4.90	3.4
CaO	1.38	0.03	0.47	1.57	1.25	1.74	0.81	1.6
Na ₂ O	0.06	0.06	tr.	0.05	0.05	0.09	0.01	0.10
K ₂ O	0.01	0.00	0.00	0.12	0.01	0.02	0.01	0.03
H ₂ O ⁺	n.d.	0.31	0.09	n.d.	0.07	—	0.08	—
H ₂ O ⁻	0.04	0.42	0.14	0.06	0.23	—	0.03	—
Total	99.81	100.25	100.21	100.18	100.06	99.7	99.83	99.7
Fe	56.6	57.7	59.5	62.5	72.0	75.2	82.2	85.4
Mg	40.5	42.2	39.5	34.1	25.2	20.9	15.9	10.9
Ca	2.9	0.1	1.0	3.4	2.8	3.9	1.9	3.7
En	41.6	41.1	40.0	35.3	25.7	21.8	16.2	11.4
<i>Cell parameters and optical properties</i>								
<i>a</i> Å	18.334	18.307	18.320	18.337	18.364	18.384	18.401	18.426
<i>b</i> Å	8.916	8.917	8.932	8.957	9.003	9.006	9.021	9.040
<i>c</i> Å	5.214	5.210	5.215	5.221	5.232	5.228	5.238	5.246
D	3.62	—	3.65	3.68	3.75	—	3.83	—
γ	1.734	1.738	1.737	1.743	1.758	—	1.763	—
2 <i>V</i> _{α}	—	57°	56°	58°	66°	—	78°	—
<i>Numbers of metal ions on the basis of 6(O)</i>								
Si	1.943	1.895	1.876	1.892	1.949	1.982	1.954	1.987
Al	.057	.105	.124	.108	.051	.010	.046	.010
Al	.045	.051	.007	.009	.015	—	.058	—
Fe ³⁺	.028	.045	.059	.048	.034	.072	.018	.130
Mg	.785	.779	.792	.664	.492	.412	.306	.214
Ti	.005	.028	.009	.031	.010	—	.003	—
Fe ²⁺	1.054	1.059	1.123	1.138	1.354	1.401	1.542	1.415
Mn	.017	.010	.009	.031	.033	.018	.020	.111
Na	.005	.005	—	.005	.004	.007	.001	.008
Ca	.057	.001	.020	.067	.055	.077	.037	.072
K	—	—	—	.006	—	.001	.001	.002

ite series, Nambran Paramba, Tinnevely, Madras (Howie, 1955).

V.2. Eulite, basic garnetiferous granulite, Fästningsberget, Varberg, Sweden (Howie and Subramaniam, 1957).

H.4. Eulite, two pyroxene-calcite-quartz rock, Mount Reed area iron formation, northern Quebec (Kranck, 1961). Anal. S. H. Kranck.

UG.29a. Eulite, charnockitic adamellite, Oribo Gorge, Marble Delta, Natal (Howie, 1958).

A.50. Eulite, quartz-magnetite-two pyroxene rock, Mount Reed area iron formation, northern Quebec (Kranck, 1961). Anal. S. H. Kranck.

Analyses except 1, 35, J.32, 3, 12700, H.4 and A.50 by R. A. Howie.

(Text continued from page 215)

Although ideally simply (Mg, Fe)SiO₃, all orthopyroxenes contain appreciable amounts of other ions substituting for the metal ions in the structure: this is particularly true for the orthopyroxenes which have crystallized under the P,T conditions of the granulite facies. The principal ions thus entering their structure are Al³⁺, Ti⁴⁺, Fe³⁺, Cr³⁺, Mn²⁺, Ca²⁺ and Na⁺: the interionic distances for the appropriate octahedral and tetrahedral positions are given in Table 4. It will be seen from Tables 1 to 3 that Na is

TABLE 4. APPROXIMATE INTERIONIC DISTANCES

Six-fold coordination (after Green, 1959)	
Mg ²⁺ . . . O ²⁻ = 2.06 Å	Al ³⁺ . . . O ²⁻ = 1.91 Å
Fe ²⁺ . . . O ²⁻ = 2.14 Å	Cr ³⁺ . . . O ²⁻ = 2.03 Å
Ca ²⁺ . . . O ²⁻ = 2.39 Å	Fe ³⁺ . . . O ²⁻ = 2.04 Å
Mn ²⁺ . . . O ²⁻ = 2.20 Å	Ti ⁴⁺ . . . O ²⁻ = 2.08 Å
Na ⁺ . . . O ²⁻ = 2.37 Å	
Four-fold coordination (Smith, 1954)	
Si ⁴⁺ . . . O ²⁻ = 1.60 Å	Al ³⁺ . . . O ²⁻ = 1.78 Å

virtually absent, Cr³⁺ is also very low (Table 1, 20486; see also Howie, 1955, where for 13 orthopyroxenes Cr varies from 300 to <2 ppm). Ti⁴⁺ is low and relatively constant in amount at around 0.002 to 0.006 per six oxygens: where it has a higher value this may be due to its occurrence as exsolved crystallites of rutile or ilmenite, giving rise to the schiller effect visible in some specimens. Mn²⁺ is also relatively constant at 0.015 to 0.030, and becomes important only at the iron-rich end of the series. The chief substituent ions are thus Al³⁺, Fe³⁺ and Ca²⁺. Al³⁺ may exist in four-fold coordination partly replacing Si⁴⁺ or in six-fold coordination replacing Mg²⁺ or Fe²⁺. In the former case the relatively larger interionic distance of 1.78 Å as compared with 1.60 Å for Si⁴⁺ and O²⁻ would be expected to bring about an increase in the cell parameters, while the substitution of Al³⁺ in the octahedral position giving an Al³⁺ . . . O²⁻ distance of 1.91 Å compared with that of Mg²⁺ and Fe²⁺ or 2.06 and 2.14 Å respectively will clearly lead to a decrease in cell parameters. In re-calculating the chemical analyses on the basis of six oxygens, sufficient Al³⁺ (where available) has been placed with Si⁴⁺ to make the Z group exactly 2.00, the remainder of the Al³⁺ being placed in the Y group. The resulting distribution of Al³⁺ between the tetrahedral and octahedral positions does not lead to significantly different results from those obtained by using the recalculation method of Hess (1949). The replacement of Fe²⁺ by Fe³⁺ would lead to a decrease in interionic distances though the Fe³⁺ . . . O²⁻ distance is only slightly less than that of Mg²⁺ . . . O²⁻. The Ca²⁺ ion, however, is considerably larger than any others in the orthopyroxene structure and its entry may be expected to cause an increase in the cell parameters: the entry of Mn²⁺ would give a similar effect.

It was initially supposed that the partial replacement of ions in the octahedral position by others of different size would cause variations in all three

parameters, *a*, *b* and *c*. Hess (1952), however, recorded the empirical results for Bushveld type igneous pyroxenes and showed that the introduction of the larger Ca²⁺ ion increased only the *a* dimension, whereas the substitution of the smaller Al³⁺ decreased only the *b* dimension. The expected increase in cell parameters due to the substitution of Al³⁺ for Si⁴⁺ in the tetrahedral position was not observed by Hess, nor is it apparent from the present data.

The cell parameters are plotted in Fig. 1, where the line for *a* and the uppermost lines for *b* and *c* are those of Hess (1952). The points represent new cell parameter determinations, with the addition of repeated determinations by Professor Hess for three of the present specimens (3709, 2941 and 12700). The lower line for *c* is considered to be the best fit for the new data and indicates that the *c* dimension is less strongly affected by ion substitutions than are *a* and *b*. It should thus be possible to obtain an estimate of the Fe/Mg ratio of an orthopyroxene to approximately ±7 mol. % from a simple determination of *c*, by measuring the position of the 004 reflection (*d* ≈ 1.30 Å).

The entry of Ca²⁺ can be seen to have a slight effect in increasing the *b* dimension, e.g. for specimen V.2 (En 25.7%) with 0.055 Ca (1.25% CaO) and [Al]⁶ only 0.015 the *b* dimension lies above Hess's curve. The main control of the *b* dimension, however, appears to be the amount of substitution of Al in the octahedral position. In Fig. 1 curves have been drawn for 0.05, 0.10 and 0.15 [Al]⁶ indicating that it is possible to estimate the amount of Al³⁺ entering the octahedral position in an orthopyroxene if the Fe/Mg ratio is already known from measurement of the *c* dimension or by other means. For orthopyroxene 177/54 (En 58.7, Al₂O₃ 9.48%) the [Al]⁶ value is 0.178, giving the biggest deviation from the normal curve. It is interesting to note that the rock containing the mineral outcrops only three hundred yards from a similar rock type containing orthopyroxene A with En 61.5, Al₂O₃ 2.52%, and normal cell parameters. Thus these two orthopyroxenes closely associated both in outcrop and apparently in PT conditions of crystallization nevertheless contain entirely different amounts of alumina. It is proposed to investigate the chemistry of these particular rocks in the hope of providing a further clue to this problem.

The effect on the cell parameters of the entry of Mn²⁺ can be seen by reference to specimens H.4 (En 21.8) and A.50 (En 11.4). Both specimens contain only 0.2% Al₂O₃ and both have similar amounts of CaO and FeO, but orthopyroxene A.50 contains 3.1%

MnO compared with 0.52% in H.4. It can be seen from Table 3 and Fig. 1 that the result for specimen A.50 is to increase all three cell parameters more than the equivalent Mol. % of Fe²⁺, etc.; this is in accord with the relatively larger ionic radius of Mn²⁺.

For the *a* dimension it is clear that the entry of Al³⁺ into the octahedral position causes a decrease, but the relationship is not quite as clear as for *b*.

Ramberg and De Vore (1951) concluded that, considering only the aluminium-poor orthopyroxenes, the *a* and *b* dimensions of the unit cell plotted against the Fe/Mg ratio gave curved lines which are not what one should expect unless the orthopyroxenes are not ideal mixtures between Fe and Mg silicates. The present author's contention, however, is that from the work of Hess (1952) and Kuno (1954), and from the data given here, the cell parameters show straight line variations in terms of Mg²⁺ and Fe²⁺, providing that the proportion of Mn²⁺, Ca²⁺ and Al³⁺ is constant. Ramberg and De Vore (1951) plotted curves for five analysed "alumina-poor" orthopyroxenes but of these the one causing an appreciable departure from linearity for the *a* and *b* curves contained 0.035 Al in the octahedral position. The present investigation has shown that the orthopyroxenes from charnockitic and associated granulite facies metamorphic rocks do have cell parameters consistently smaller than those from Bushveld type plutonic or volcanic rocks earlier studied. This seems to be related mainly to the increasing ability of orthopyroxenes in the granulite facies to accept greater amounts of alien ions. It is felt, however, that in cell parameter studies of this type it is essential to specify the paragenesis of the minerals, as the inclusion in one investigation of specimens from unspecified sources but including both igneous and metamorphic minerals which have crystallized under very different conditions may possibly obscure slight but important

differences in their chemistry and in their physical properties.

SPECIFIC GRAVITY

The specific gravity was determined for 35 of the analysed orthopyroxenes and the results are included in Tables 1 to 3 and in Fig. 1. This property was measured using a 10 ml pycnometer, the final reading being taken after several preliminary checks over 3 to 4 days to eliminate trapped air bubbles. That the specific gravity also varies linearly with variation in the Fe/Mg ratio is illustrated in Fig. 1, where the line drawn is taken directly from Deer *et al.* (1963) and is seen to fit reasonably well the data here presented.

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ADDENDUM

PLEOCHROISM

Earlier work has shown that the strength of the pleochroism of orthopyroxenes is not related to the iron content (Howie, 1955), nor does it appear to be simply related to the amount of Ti or Mn, or to any one trace element. The orthopyroxenes of granulite

facies rocks, however, are typically markedly pleochroic. The strongest pleochroism is shown by specimens 177/54, 2048b, 116, 3709 and 4645, all of which have more than 4% Al₂O₃, and it is here suggested that the strength of the pleochroism can be correlated with the alumina content and with the contraction of the cell parameters, *i.e.* it may be largely a physical effect.