

# Relations between cell dimensions, chemical composition, and site preference of orthopyroxene

J. V. SMITH AND D. A. STEPHENSON<sup>1</sup>

Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.

R. A. HOWIE

Department of Geology, King's College, London

AND

M. H. HEY

Department of Mineralogy, British Museum (Natural History)

**SUMMARY.** Cell dimensions have been measured from correctly indexed powder patterns of thirty natural and two synthetic orthopyroxenes. The natural specimens (mostly metamorphic) contain exsolved phases largely avoided during microprobe chemical analysis. Linear regression analysis between the cell dimensions and Mg, Al, Ca contents (ignoring minor elements) was quite unsatisfactory until a term in  $Mg^2$  was added. Two separate regression analyses for the ranges Mg 0-0.5 and 0.5-1 using only Mg, Al, and Ca were satisfactory. Olivine yielded satisfactory regressions for the whole range without a term in  $Mg^2$  (Louisnathan and Smith, 1968). The difference between olivine and pyroxene results from absence of site preference by Mg and Fe in olivine compared to strong preference in pyroxene revealed by electron density and Mössbauer studies (Bancroft, Burns, and Howie, 1967; Ghose and Hafner, 1967).

The data were recalculated by means of a new best-fit procedure developed by Hey in which the errors in the chemical and physical parameters are considered simultaneously.

Earlier measurements of *a* and *b* for plutonic pyroxenes are consistent within possible experimental uncertainties with those given here; however *a* and *b* data obtained by Kuno and by Hess on volcanic specimens are considerably higher by variable amounts. Although there are uncertainties in the Ca content and its effect on *a* and *b*, the larger dimensions probably result from lower site preference as indicated by Mössbauer studies.

Prediction of Mg, Ca, and Al from just the cell dimensions is only moderately accurate even for metamorphic orthopyroxenes.

## *Introduction (J. V. S.)*

CELL dimensions depend not only on the bulk chemical composition but also on the distribution of atoms between potential sites. Thus in favourable circumstances the cell dimensions might be used to estimate either the bulk chemical composition, the site distribution, or both. Since the petrological history of a mineral affects its chemistry, cell dimensions are useful in petrogenetic studies. However, increasing availability of the electron microprobe is leading to more rapid and more accurate estimates of bulk chemical composition of complex minerals than are available from measurement of cell dimensions. Thus for samples coarser than 5  $\mu$ , cell dimensions are becoming more valuable for their implications with respect to site preference than with respect to

<sup>1</sup> Now at Corning Glass Works, Corning, New York 14831.

bulk chemical composition. Spectral and resonance techniques are beginning to achieve major practical importance in determining site preference of suitable elements, again tending to reduce the significance of cell dimensions. A few years ago when microprobe, spectral, and resonance techniques were undeveloped, there was naturally a tendency to exaggerate the accuracy of compositions deduced from cell dimensions and earlier-used optical properties: perhaps the most important result described here is a demonstration of the low accuracy of chemical estimates made from cell dimensions of a complex silicate such as orthopyroxene.

In a pioneering paper, Ramberg and DeVore (1951) found that the  $a$  and  $b$  cell dimensions and the refractive indices of orthopyroxenes did not vary linearly with the mol fraction of enstatite obtained by bulk chemical analysis. They used these physical parameters to estimate the composition of other samples in a study of the distribution function of Mg and Fe in coexisting orthopyroxene and olivine of various plutonic and volcanic rocks. Ramberg and DeVore (p. 204) concluded from comparison of the observed Mg:Fe distributions in orthopyroxene with those of the near-ideal olivine solid solution that 'pyroxenes of intermediate composition should have a relatively greater lattice energy or less molal free energy than that which corresponds to the same mol fractions in ideal mixtures'. They expected that 'a relatively great stability in certain portions of the mix-crystal series would reflect itself—(in)—a tendency towards contraction', which should lead to an increase in the refractive indices. This expectation was confirmed by their data. In addition, they noted that large amounts of Al affected the cell dimensions and suggested that Al substituting for Mg,Fe caused  $b$  to contract while Al substituting for Si caused an expansion in the unit cell. They stated that 'it is natural that the unit cell dimensions should show some irregularities as long as the actual positions of the aluminum content of the pyroxenes are not determined'.

In an exploratory study, Hess (1952) measured the cell dimensions and optical properties of a variety of orthopyroxenes, mostly plutonic with considerable exsolved augite but some from meteorites and volcanic rocks. In contradiction to Ramberg and DeVore, he concluded that, for such plutonic orthopyroxenes typically containing about  $2\frac{3}{4}$  %  $R_2O_3$ , unit cell edges,  $\gamma$ , birefringence, and density vary linearly with Mg/(Mg+Fe+Mn) within the experimental error limits. Thus he supported the conclusion of Sahama and Torgeson (1949), on the basis of their experimental evidence that there is no heat of mixing, that orthopyroxene is an ideal mix-crystal. Ramberg and DeVore, however, had pointed out that the specimens used by Sahama and Torgeson were too close in composition to enstatite or ferrosilite to be sensitive to deviations from ideality. Hess went on to suggest that the curvature of cell dimensions versus Mg content found by Ramberg and DeVore was very probably the result of substitution by variable quantities of Ca and Al. He stated that the Mg, Fe, Al, and Ca contents of orthopyroxenes can be determined from the cell dimensions and optical properties without chemical analysis. Detailed interpretation of cell-dimension changes was given in terms of the ionic model. Unfortunately the powder diffraction pattern was incorrectly indexed, and although  $a$  and  $b$  were correctly derived,  $c$  is incorrect. Stephenson, Smith, and Howie (1968) unfortunately ascribed the indexing error to Ramberg and

DeVore. The error was carried over into the work of Kuno (1954) and of Howie (1963).

Hess (1952) noted that volcanic orthopyroxenes might have optical properties different from those of plutonic specimens. Kuno (1954) stated that, unlike plutonic orthopyroxenes, volcanic specimens have not exsolved augite and thus the effect of Ca on their physical properties can be determined. He proposed, on the basis of new measurements of thirteen volcanic and six plutonic and metamorphic specimens, that the Mg content could be estimated directly from  $\gamma$ , and that the Ca and Al contents could then be estimated from  $a$  and  $b$ . The only difference found between volcanic orthopyroxenes and the plutonic specimens with exsolved material was in  $2V$ , and this was ascribed either to difference in Ca content (following Hess) or to order-disorder. The type of order-disorder was not specified.

Howie (1963) determined the bulk chemical composition and the cell dimensions of forty-six orthopyroxenes from metamorphic rocks, the majority from the granulite facies. The cell dimensions  $a$  and  $b$  were smaller than those obtained by Hess and by Kuno for igneous orthopyroxenes with the same  $Mg/(Mg+Fe+Mn)$  ratio: this was thought to result particularly from differences in the amount of Al in the octahedral sites, and also in the  $Fe^{2+}$ , Ti, Ca, and Mn contents. The departure from linearity of the cell dimensions reported by Ramberg and DeVore, and taken by them as evidence of the non-ideal nature of the orthopyroxene-mixed crystal series, was interpreted rather as the effect of variable Al substitution. Detailed interpretation of the cell dimension changes in terms of radii of substituting ions was given. Brown (1968) has recalculated Howie's data using a parabolic relation.

Winchell and Leake (1965) presented an abstract in which regression estimates were given for the refractive indices, specific gravity, and cell dimensions of a compilation of literature data on natural orthopyroxenes. Presumably many include exsolved phases, for which the bulk chemical analyses were not corrected. Leake (1968) plotted 123 determinations of  $\alpha$  and 205 of  $\gamma$  against  $mg = Mg/(Mg+Fe+Mn)$ , together with values of  $2V$  for 19 volcanic and 147 other pyroxenes. Unlike earlier workers he did not distinguish between the optical properties of volcanic and plutonic specimens. By using reduced major axis regression he found a standard error in  $mg$  of 0.05 when estimated from the refractive indices and 0.08 when estimated from  $2V$ .

The first conclusive evidence that orthopyroxenes do not form a single, ideal solid solution was obtained by Ghose (1965), who showed from electron densities derived from X-ray diffraction data of a metamorphic orthopyroxene that most of the Fe was in octahedral site<sup>1</sup>  $M_2$  and most of the Mg correspondingly in  $M_1$ . A series of studies using Mössbauer resonance of the  $Fe^{57}$  gamma rays has confirmed the site preference of Fe in  $M_2$ , though early measurements made at room temperature were hampered by poor resolution (Bancroft, Burns, and Howie, 1967; Bancroft and Burns, 1967; Dundon and Walter, 1967; Evans, Ghose, and Hafner, 1967; Ghose and Hafner, 1967). Resolution at low temperatures is much improved (Virgo and Hafner, 1968), and precise data are forthcoming. The preliminary data suggest that in most well-annealed specimens (plutonic and regional metamorphic) site preference of Fe for  $M_2$  is so

<sup>1</sup> Site nomenclature after Burnham (1967).

great that the orthopyroxenes approximate to two solid solution series:  $M_1 = \text{Mg}$ ,  $M_2 = (\text{Mg,Fe})$ , and  $M_1 = (\text{Mg,Fe})$ ,  $M_2 = \text{Fe}$ . In natural quenched (volcanic) specimens site preference is reduced, though still rather high. Site preference can be decreased by heating for a few hours or days above 1000 °C.

This demonstrated variation in site preference suggests that cell dimensions and optical properties of orthopyroxenes should vary with the petrological environment, even when account has been taken of bulk chemical variations. Additional effects may also occur; thus the fractionation of Al and other minor elements is probably related to the fractionation of Mg and Fe.

Recent thermodynamic and synthesis studies have extended the work of Ramberg and DeVore to include ideal and non-ideal distribution between sites in just a single mineral or between sites in a mineral pair (Mueller, 1962; Grover and Orville, 1968). Banno and Matsui (1966) have considered the distribution of Fe and Mg between ortho- and clino-pyroxene, while Mueller (1964), Speidel and Osborn (1967), and Nafziger and Muan (1967) have considered the distribution between pyroxene and olivine. The distribution data appear to be explained by non-ideal behaviour of orthopyroxene when the *bulk* properties across the entire series are considered, and by near-ideal behaviour over each half-series when individual  $M_1$  and  $M_2$  sites are considered.

The present study was begun after completion of electron microprobe analyses of forty-eight chemically analysed orthopyroxenes (Howie and Smith, 1966). Unlike the earlier bulk chemical analyses the microprobe analyses gave a fairly good approximation to the composition of the host orthopyroxene, uncontaminated by the included augite, ilmenite, and other impurities. Thus for the first time it was possible to correlate the cell dimensions with the actual composition of the orthopyroxene. Even so, the complexities caused by the presence of minor elements and the possible differences in site preference have resulted in considerable difficulty in interpretation.

#### *Experimental (D. A. S.)*

Cell dimensions were determined for thirty of the samples previously used for microprobe analysis. The diffraction angles were measured with a diffractometer using smear mounts mixed with Spec-pure silicon assumed to have  $a$  5.43062 Å. Cu- $K\alpha$  radiation was used for Mg-rich specimens and Fe- $K\alpha$  for Fe-rich ones. Indexing was checked with intensities derived from single-crystal Weissenberg photographs of selected specimens. A complete indexing of a synthetic ortho-enstatite was given by Stephenson, Sclar, and Smith (1966; note, observed  $d$  for 131 is 2.5299 not 2.6299). Table I lists observed  $2\theta$  values for selected diffraction spectra of this specimen and seven natural orthopyroxenes with Mg contents of 0.88 (Cu- $K\alpha_1$  radiation), 0.77, 0.62, 0.45, 0.33, 0.24, and 0.16 (all with Fe- $K\alpha_1$  radiation). Most strong lines of most unknown orthopyroxenes should be indexable by comparison with the above listed data: however, it should be noted that variable Ca and Al contents, and variable site preference of Mg and Fe, cause significant changes that cannot be accounted for by a simple interpolation on the basis of merely the Mg content. Intensities vary greatly across the mineral series, and will also depend on the method of measurement if preferred orientation is present.

TABLE I. Listing of observed  $2\theta$  values and  $hkl$  indices for selected orthopyroxenes. The values for OEN and SAG are for filtered Cu radiation, all others for filtered Fe radiation

$hkl$	OEN	SAG	E-21	E-22	E-25	7725	H-4	UG29a
210	13.99	—	—	—	—	17.32	17.31	17.28
400	—	—	—	24.44	24.45	24.34	24.33	24.29
020	20.13	20.08	—	—	—	—	—	—
211	—	—	—	27.77	27.65	27.63	—	—
121	27.02	26.96	34.02	33.88	33.73	33.62	33.66	33.55
420	28.17	28.13	35.54	35.44	35.33	35.15	35.06	35.01
221	28.33	—	—	—	—	—	—	—
321	30.42	30.36	38.39	38.25	38.12	37.99	37.90	37.84
610	31.13	31.10	39.36	39.27	39.19	39.07	39.01	38.96
511	31.68	31.63	40.03	39.92	39.79	39.73	39.74	39.61
230	31.98	—	—	—	—	—	—	—
421	33.13	33.09	41.89	41.77	41.60	41.49	41.40	41.32
131	35.45	35.39	44.87	44.66	44.46	44.27	44.13	44.05
611	—	—	—	45.15	45.03	44.97	44.91	44.87
202	36.04	35.98	45.62	45.48	45.32	45.31	—	45.20
521	36.37	36.34	46.10	45.96	45.81	45.65	45.52	45.42
302	37.80	—	—	—	47.50	—	—	—
331	38.22	—	—	—	—	—	—	—
800	39.54	39.34	—	—	—	—	—	—
402	40.08	—	—	—	—	—	—	—
431	40.44	—	—	—	—	—	—	—
630	42.81	42.75	54.46	54.28	54.12	54.01	53.72	—
531	43.21	43.11	55.00	54.77	54.53	54.39	54.22	54.11
721	43.98	—	56.01	55.90	55.69	—	55.53	—
512	44.11	43.99	—	—	—	—	—	—
141	44.98	44.78	—	56.95	56.70	56.53	{ 56.25 } { 56.46 }	56.36
820	44.76							
440	45.73	45.65	58.30	58.06	57.80	57.54	57.25	57.18
241	45.83							
631	46.41	46.35	59.19	58.98	58.75	58.56	58.44	58.29
821	48.26	—	—	—	—	—	—	—
332	49.21	—	—	—	—	—	—	—
702	49.66	—	—	—	—	—	—	—
10.1.0	51.13	51.07	—	65.44	—	—	64.92	64.83
541	51.60	51.44						
250	52.85	52.74	67.77	67.51	67.11	66.76	66.42	66.25
831	53.90	53.78	69.19	—	—	—	—	—
812	54.63	—	—	—	—	—	—	—
023	57.31	—	—	—	—	—	—	—
10.2.1	57.50	—	—	—	—	—	—	—
922	57.76	—	—	—	—	—	—	—
413 } 931 }	58.08	57.98	74.95	74.75	74.50	74.29	74.08	73.91
840	58.22	—	—	—	—	—	—	—
650	60.66	60.55	78.54	78.23	—	77.46	77.15	76.98
12.0.0	60.96	60.86	79.04	78.87	78.69	78.52	78.45	78.28
10.3.1	62.54	62.43	81.19	80.99	80.71	80.49	80.30 } 80.46 }	80.09
060	63.22	63.11	82.09	81.67	81.21	80.76		
352	65.86	—	—	—	—	—	—	—
11.0.2	67.03	—	—	—	—	—	—	—
11.3.1	67.28	67.18	88.00	87.75	87.49	87.24	87.01	86.83
12.3.1	72.28	72.20	—	—	—	—	—	—
12.1.2	72.95	—	—	—	—	—	—	—
14.1.0	73.48	—	—	—	—	—	—	—
214 } 10.5.0 }	74.88	74.76	—	—	—	—	—	—
304	74.98	—	—	—	—	—	—	—
16.0.0	85.08	—	—	—	—	—	—	—
12.6.0	93.66	—	—	—	—	—	—	—
14.5.0	94.70	—	—	—	—	—	—	—

TABLE II. Contents of *M* sites, in atomic fractions, with two estimates of Ca (see text), and observed cell dimensions of orthopyroxenes. The figures are the assessed probable experimental errors in the last significant figure shown, as derived from the least squares fit using Burnham's (1962) computer programme

Specimen	Mg	Ca av.	Ca min.	Al	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i>
Syn. En.	1·000	0·000	0·000	0·000	18·225 (1)	8·816 (1)	5·174 (1)	831·3 (1)
Sag	0·880	0·002	0·002	0·015	18·254 (4)	8·831 (2)	5·191 (3)	836·8 (5)
Y29	0·805	0·039	0·024	0·041	18·274 (4)	8·834 (2)	5·195 (2)	838·6 (3)
R62	0·805	0·005	0·004	0·078	18·257 (1)	8·816 (1)	5·190 (2)	835·3 (3)
Y12	0·824	0·004	0·003	0·020	18·256 (3)	8·850 (1)	5·196 (2)	839·4 (3)
20486	0·773	0·010	0·010	0·063	18·264 (4)	8·826 (2)	5·192 (3)	836·9 (4)
E21	0·775	0·009	0·009	0·035	18·258 (2)	8·844 (1)	5·195 (1)	838·9 (2)
H66	0·726	0·006	0·006	0·079	18·257 (2)	8·826 (1)	5·196 (2)	837·2 (3)
R104	0·736	0·004	0·004	0·020	18·268 (3)	8·856 (1)	5·197 (2)	840·8 (4)
4645	0·682	0·007	0·006	0·083	18·261 (2)	8·834 (1)	5·203 (2)	839·4 (2)
E22	0·618	0·015	0·014	0·024	18·286 (2)	8·879 (1)	5·212 (2)	846·3 (2)
R136	0·600	0·007	0·006	0·038	18·286 (2)	8·884 (1)	5·211 (1)	846·5 (2)
A	0·590	0·008	0·007	0·046	18·286 (2)	8·873 (1)	5·208 (2)	845·0 (3)
SP18	0·573	0·005	0·004	0·059	18·283 (2)	8·868 (1)	5·213 (1)	845·1 (3)
177/54	0·538	0·002	0·002	0·179	18·262 (6)	8·814 (2)	5·207 (3)	838·1 (5)
2270	0·576	0·012	0·010	0·014	18·299 (3)	8·897 (1)	5·217 (2)	849·4 (4)
R96	0·541	0·009	0·007	0·090	18·294 (4)	8·865 (2)	5·211 (2)	845·2 (4)
2941	0·513	0·008	0·007	0·064	18·294 (3)	8·881 (2)	5·216 (2)	847·4 (4)
137/59	0·491	0·003	0·003	0·091	18·290 (3)	8·873 (1)	5·217 (1)	846·7 (2)
7286	0·484	0·016	0·014	0·026	18·323 (6)	8·919 (2)	5·226 (3)	854·1 (5)
Y23	0·481	0·011	0·010	0·021	18·323 (3)	8·915 (2)	5·225 (3)	853·5 (4)
E25	0·447	0·016	0·015	0·029	18·327 (3)	8·922 (2)	5·231 (2)	855·5 (3)
4642A	0·401	0·013	0·010	0·025	18·323 (2)	8·936 (1)	5·226 (2)	855·7 (2)
400	0·381	0·016	0·014	0·016	18·340 (2)	8·947 (1)	5·231 (1)	858·4 (2)
15	0·363	0·020	0·019	0·018	18·355 (3)	8·966 (2)	5·226 (3)	860·1 (5)
725	0·331	0·017	0·015	0·014	18·359 (4)	8·967 (2)	5·232 (3)	861·2 (5)
1002	0·262	0·013	0·011	0·021	18·386 (3)	8·985 (1)	5·232 (2)	864·3 (3)
H4	0·237	0·017	0·013	0·003	18·379 (3)	9·001 (1)	5·238 (4)	866·6 (5)
V2	0·231	0·020	0·017	0·009	18·382 (3)	9·001 (2)	5·240 (4)	866·9 (5)
XI/132	0·205	0·021	0·019	0·010	18·395 (2)	9·015 (1)	5·244 (3)	869·6 (4)
UG29a	0·163	0·021	0·013	0·010	18·405 (3)	9·024 (2)	5·242 (2)	870·7 (4)
Syn. Fs	0·000	0·000	0·000	0·000	18·431 (4)	9·080 (2)	5·238 (1)	876·5 (4)

Recent development of computer programmes for simulating powder patterns from crystal-structure parameters should permit accurate delineation of intensity changes caused by substitution of cations (Borg and D. K. Smith, 1967; Jahanbagloo and Zoltai, 1967; D. K. Smith, 1967). Unfortunately there are at present too few precise determinations of atomic co-ordinates to permit really accurate simulation. Perhaps it may be possible to estimate the site preference of Mg and Fe from the intensities of powder patterns if careful measurements are made, with especial attention to reduction of preferred orientation; such estimates would be aided by determination of the chemical composition from electron microprobe analysis.

The cell dimensions (table II) were obtained by a least-squares minimization of the calculated and observed values of  $1/d^2$ , following the method of J. V. Smith (1956), augmented and programmed for computers by Burnham (1962). The relative error in

$c$  is about twice that of  $a$  and  $b$  because there are fewer suitable high-angle reflections dependent on large values of  $l$ .

The 004 reflection, previously used by Hess, by Kuno, and by Howie to yield  $c$ , is so weak on Weissenberg films that it is not clearly visible on powder patterns. Comparison of the present cell dimensions with those previously measured on the same specimens by Howie shows good agreement with  $a$  and  $b$  for many specimens, but some discrepancies are greater than the combined experimental errors. Perhaps some numerical errors crept into Howie's work, but alternatively both measurements may be accurate and the deviations may result from taking different fractions of chemically zoned material.

The cell dimensions of synthetic ortho-enstatite were taken from Stephenson, Sclar, and Smith (1966), while those for a synthetic orthoferrosilite were kindly supplied by C. W. Burnham from extrapolation of back-reflection Weissenberg data.

#### *Regression analysis (J. V. S., D. A. S.)*

In setting up the mathematical analysis, it was necessary to make many simplifying assumptions. Some can be justified by crystal-chemical arguments, but others may be invalid. Although the three independent cell dimensions could be expressed in terms of as many chemical parameters as are available (Winchell and Leake, 1965), lack of precise knowledge on the distribution of all minor elements, and the small range of most minor elements in orthopyroxenes, suggests that only six chemical variables need be considered—Mg, Fe, Ca, Al, Cr, and Mn. The minor elements Ti, V, Ni, Zn, Na, and K occur in such small quantities that they can be neglected. Cr occurs up to 0.5 wt % in some Mg-rich orthopyroxenes. Mn occurs up to 1.0 wt % with a tendency to be greater in Fe-rich specimens. Since the ionic radii of Cr and Mn are not too grossly different from that of Fe, Cr and Mn were added to Fe, reducing the number of chemical variables to four. For simplicity the other minor elements were added to Fe also.

Aluminium poses a major problem. Typically a chemical analysis is recalculated to 6 oxygens and Al is added to Si to give a total of 2 for the tetrahedral site. The remaining Al (if any) is allocated to the octahedral ( $M$ ) sites. If all other substituents in Si sites were tetravalent (e.g. Ti), and those in octahedral sites were divalent (e.g. Mn and Ca), Al should be equally proportioned between tetrahedral and  $M$  sites to maintain charge balance. Examination of the selected analyses in Deer, Howie, and Zussman (1963) shows that there are often significant amounts of  $\text{Fe}^{3+}$ , which might be expected to occur in  $M$  sites since Al should preferentially replace Si. Thus charge balance requires that  $(\text{Al} + \text{Fe}^3)$  in  $M$  sites should equal Al in tetrahedral sites. Although there are some discrepancies, partly attributable to errors in the chemical analysis and partly attributable to other minor substituents, this relationship is fairly well obeyed by many chemical analyses. Fig. 1*a* illustrates the relation as calculated for the analyses in Howie (1963) (analytical errors might result from the common over-estimation of Al at the expense of other elements, especially Si and Fe, and from difficulty of dissolving ferrous iron without some conversion to ferric iron). Thus the statistical analysis should consider two separate parameters for Al since the cell

dimensions should be affected quite differently by occupation of tetrahedral and octahedral sites: in addition a parameter for  $\text{Fe}^{3+}$  distinct from that of  $\text{Fe}^{2+}$  should be used. Electron microprobe analysis using K spectra does not distinguish between ferric and ferrous iron. Furthermore the analytical accuracy is not sufficiently good to give a precise allocation of Al to the two sites. Although real differences between the Al contents of the two sites undoubtedly exist (fig. 1b) regrettably it was decided to represent Al by only one parameter, and to combine  $\text{Fe}^{3+}$  with  $\text{Fe}^{2+}$ . For convenience, the total Al content from microprobe analysis was divided by 2 and the halved value assigned to the octahedral sites.

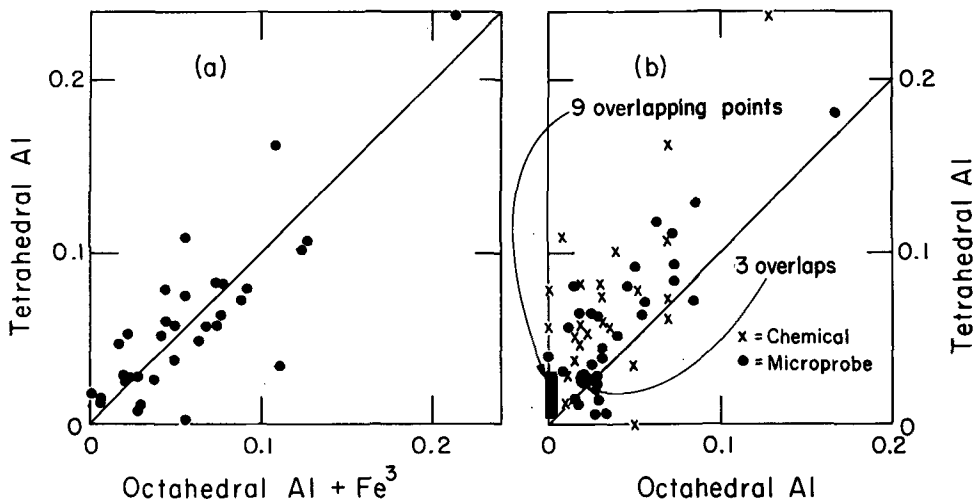


FIG. 1. Octahedral Al or Al+ $\text{Fe}^{3+}$  v. tetrahedral Al for orthopyroxenes (see text).

If all the tetrahedral and octahedral sites in orthopyroxene are now assumed to be fully occupied, the major elements Si, Al, Mg, Ca, and Fe (plus minor elements) can be reduced to three effective parameters *so long as* site preference is ignored. This results from the obvious crystal-chemical assumption that Mg, Ca, and Fe (plus minor elements) go into octahedral sites (ferric iron was not distinguished from ferrous iron in the microprobe analysis, and anyway is probably pre-empted from entering tetrahedral sites by Al). Thus the parameters Mg, Ca, Al (= half total Al) specify the octahedral site, and Fe (plus minor elements) =  $1 - (\text{Mg} + \text{Ca} + \text{Al})$ . The tetrahedral site is automatically specified by  $\text{Si} + \text{Al} = 1$ .

The presence of relatively fine lamellae of exsolved augite caused considerable difficulty in estimating the Ca content of the host orthopyroxene by microprobe analysis (Howie and Smith, 1966). They stated 'distance profiles were made for 100  $\mu$  on each of seven crystals at a fixed wavelength. In addition to "spikes" for the augite lamellae, there were continuous variations of signal, suggesting non-uniformity of the calcium content of the orthopyroxene. Such apparent composition variations might be genuine (perhaps controlled by diffusion between augite and orthopyroxene) or might result merely from averaging of orthopyroxene and submerged augite inclusions.



Although no specific tests were made, the ubiquity of the apparent composition variations and the rarity of lamellae in some specimens suggest that the calcium content of orthopyroxene is variable and should be studied in detail. Distance profiles for aluminum also showed both continuous and discontinuous variations'. For the present purpose the true average Ca and Al contents are needed for regression with the cell dimensions. Since exsolved augite is likely to have a fairly similar Al content to that of the host orthopyroxene, the mean observed Al content is likely to be reasonably close to the true value. For Ca, however, the mean Ca content even for regions excluding the 'spikes' may be affected seriously by the high Ca-content of exsolved augite. Consequently calculations were carried out both for the average value of Ca (excluding spikes) and for the lowest value of Ca. One specimen, Y29 from the Stillwater Igneous Complex, had so many fine exsolved lamellae that estimation of Ca was particularly difficult. Since the indicated Ca-content of this orthopyroxene is greater than that of other specimens, calculations were made both with and without this specimen.

Because all the present specimens are from geological environments for which annealing was prolonged, it was thought that all would have strong preference, and that the site preferences would plot fairly smoothly with increasing Mg-content. Furthermore it was thought that the minor elements would show a related site preference. Probably Al correlates with Mg while Ca and Mn correlate with Fe.

An initial multivariate regression between  $a$ ,  $b$ ,  $c$  and Mg, Al, and Ca, utilizing all specimens, was unsatisfactory because of significant positive residuals for intermediate values of Mg and negative residuals for both small and large values. This result was expected since site preference should lead to different coefficients according as Mg is in  $M_1$  or in  $M_2$ , etc.

Satisfactory regressions were obtained by either splitting up the data into two groups of 18 specimens with  $Mg < 0.5$  and 14 specimens with  $Mg > 0.5$  or by retaining all 32 specimens in one group but adding a term in  $Mg^2$ . Table III gives the resulting coefficients of the equations, while fig. 2 shows the residuals. The single regression with the extra term in  $Mg^2$  gives larger residuals than the pairs of regressions omitting  $Mg^2$ . However, this is partly the result of the former using fewer adjustable coefficients; although no numerical justification is offered, it would be unwise to claim that one is statistically better than the other. Indeed the true situation should lie between these two extreme approximations since the gamma-ray resonance data for Fe indicate strong but not complete site preference.<sup>1</sup>

Detailed examination of table III shows that the terms in  $Mg^2$  are significant. When the minimum value of Ca replaces the average value, the coefficients for Ca change considerably but those for the other chemical parameters change only slightly. The corresponding coefficients for the two regressions which omit  $Mg^2$  are often quite different suggesting that cation substitution has different physical effects in the two  $M$  sites. The crystal-chemical significance of these results will not be discussed here since a more comprehensive statistical analysis will be given later.

However, it is convenient here to compare cell parameters in the literature with

<sup>1</sup> After completion of the regression analysis, it was realized that MgFe would have been a better parameter than  $Mg^2$ , but since  $Fe \approx 1-Mg$ , the difference is unlikely to be significant.

TABLE III. Regression equations

<i>Variable = p+qMg+rMg<sup>2</sup>+sCa+tAl</i>							
	<i>p</i>	<i>q</i>	<i>r</i>	<i>s</i>	<i>t</i>	<i>R</i>	$\sigma$
<i>Ca average: 32 observations</i>							
<i>a</i>	18.4357	-0.303	0.101	0.77	-0.213	0.9900	0.0014
		28	26	21	48		
<i>b</i>	9.0831	-0.3767	0.1137	0.208	-0.562	0.9982	0.0008
		161	151	119	28		
<i>c</i>	5.2416	-0.0103	0.0583	0.129	-0.082	0.9846	0.0006
		119	111	88	21		
<i>V</i>	877.65	-52.2	6.4	78	-76.9	0.9979	0.15
		2.9	2.7	22	5.1		
<i>Ca minimum: 32 observations</i>							
	18.4352	-0.318	0.118	1.16	-0.192	0.9903	0.0014
		29	27	30	49		
<i>b</i>	9.0826	-0.3830	0.1205	0.371	-0.552	0.9983	0.0008
		163	156	170	59		
<i>c</i>	5.2415	-0.0128	0.0555	0.194	-0.079	0.9847	0.0006
		123	118	129	21		
<i>V</i>	877.56	-54.0	8.4	123	74.4	0.9980	0.147
		2.9	2.8	31	5.1		
<i>Variable = p+qMg+rCa+sAl</i>							
	<i>p</i>	<i>q</i>	<i>r</i>	<i>s</i>	<i>R</i>	$\sigma$	
<i>Mg 1.0-0.5: Ca average: 18 observations (set A)</i>							
<i>a</i>	18.3751	-0.1436	0.582	-0.182	0.9747	0.0011	
		95	135	31			
<i>b</i>	9.0221	-0.2056	-0.015	-0.550	0.9910	0.0009	
		80	114	27			
<i>c</i>	5.2665	-0.0891	0.078	-0.696	0.9772	0.0006	
		54	78	181			
<i>V</i>	872.78	-40.6	37.8	-72.2	0.9916	0.17	
		1.4	20.6	4.8			
<i>Mg 1.0-0.5: Ca minimum: 18 observations (set C)</i>							
<i>a</i>	18.3709	-0.1399	0.881	-0.175	0.9719	0.0020	
		101	0.225	34			
<i>b</i>	9.0229	-0.2061	-0.069	-0.552	0.9910	0.0009	
		81	179	27			
<i>c</i>	5.2661	-0.8887	0.107	-0.069	0.9768	0.0006	
		56	124	18			
<i>V</i>	872.59	-40.41	51.8	-71.9	0.9911	0.18	
		1.51	33.5	5.0			
<i>Mg &lt; 0.5: Ca average: 14 observations (set E)</i>							
<i>a</i>	18.4316	-0.243	0.68	-0.245	0.9861	0.0011	
		21	40	151			
<i>b</i>	9.0771	-0.3194	0.27	-0.524	0.9970	0.0013	
		133	26	97			
<i>c</i>	5.2384	0.0414	0.515	-0.030	0.9407	0.0008	
		82	161	60			
<i>V</i>	876.29	-48.8	144	-65.3	0.9970	0.20	
		2.0	39	14.4			

TABLE III. *Regression equations (cont.)*

Variable	$p+qMg+rCa+sAl$					
	$p$	$q$	$r$	$s$	$R$	$\sigma$
Mg < 0.5: Ca minimum: 14 observations (set F)						
$a$	18.4321	-0.249	0.87	-0.225	0.9867	0.0020
		22	48	151		
$b$	9.0764	-0.3242	0.45	-0.497	0.9973	0.0013
		134	30	93		
$c$	5.2396	-0.0436	0.57	-0.034	0.9310	0.0009
		94	21	66		
$V$	876.47	-49.88	1.79	-62.7	0.9972	0.19
		2.02	45	14.1		

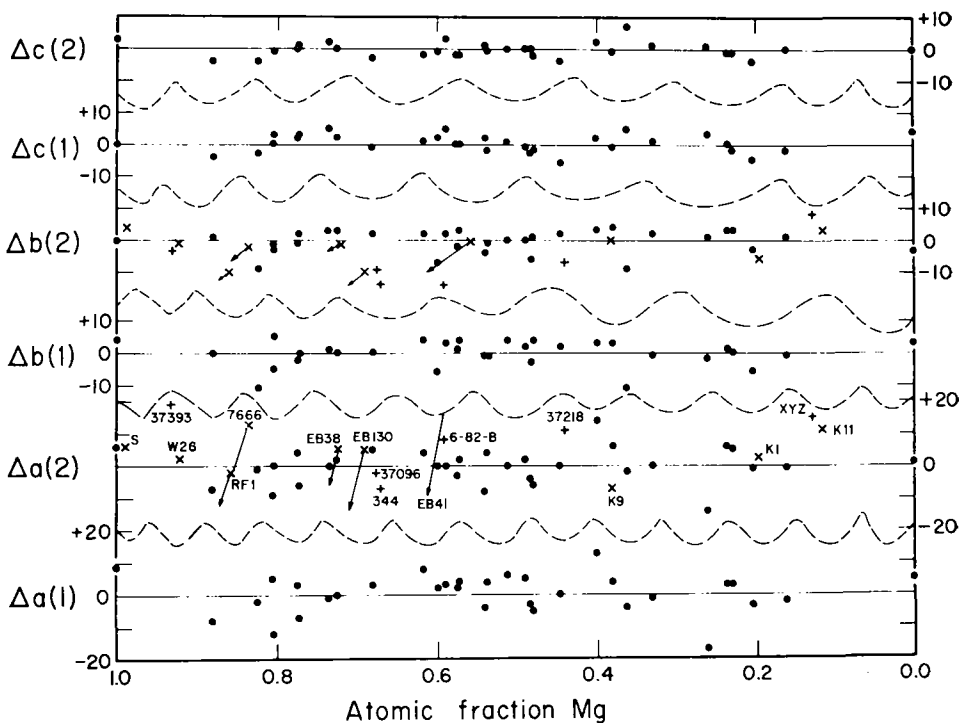


FIG. 2. Residuals from the regression equations: (1) range Mg 1-0, using a term in  $Mg^2$ ; (2), separate linear equations for ranges Mg 1-0.5 and Mg 0.5-0. ●, data for the specimens of table II; × and + for the plutonic and metamorphic specimens of table IV (for arrows see text).

those given here. Table IV lists literature data for those specimens whose bulk chemical composition was determined by chemical analysis. Five of these definitely contain augite lamellae as identified optically; others may contain unidentified lamellae. The composition of the host orthopyroxene was estimated by extrapolating the bulk composition from an arbitrary composition  $\text{Di}_{50}\text{Wo}_{50}$  to a Ca content of 0.005–0.006, and assuming no change in Al. For geologically annealed specimens, the residuals between the observed cell dimensions and values calculated from the bulk chemical data using the equations in table III are given in fig. 2, together with arrows showing the correction for exsolved augite. The cell dimensions  $a$  and  $b$  given by Ramberg and DeVore were adjusted to give the best fit for 14.5.0, the measured reflection with the highest diffraction angle. Considering the possible uncertainties in the earlier measurements of cell dimensions, and in the use of bulk chemical compositions, the agreement is not unreasonable.

If volcanic specimens have been quenched rapidly enough to overcome the tendency towards annealing found in regional metamorphic and igneous plutonic specimens, their cell dimensions need not fit the equations obtained by regression of data for the latter. Since the site preference should be less in the volcanic specimens, corresponding to greater disorder, the cell dimensions should be slightly greater and the refractive indices slightly smaller. Fig. 3 (p. 105) compares the residuals of the volcanic specimens measured by Hess and by Kuno with those for the present suite of specimens, mostly metamorphic. The volcanic specimens tend strongly to have larger  $a$  and  $b$  cell dimensions. The rather large spread of data is to be expected since the rate of cooling will be quite variable. Although these data agree nicely with the supposition of greater disorder in the volcanic specimens, it is possible that other effects might be the cause. Thus the Ca-content of the volcanic specimens tends to be higher than in the metamorphic specimens. Since there is some doubt about the actual Ca-content of the metamorphic specimens, residuals were calculated using equations both for average Ca and lowest Ca. The resulting change for the volcanic specimens is relatively small, preserving the general tendency towards larger cell dimensions. It was assumed that the bulk chemical estimates of Ca are accurate, and that the volcanic orthopyroxene contains no exsolved augite. No information is available on the accuracy of the chemical analyses though it is likely that the analyses used by Hess (1952) and by Kuno (1954) are good. If the Ca content is reduced to take account of exsolved augite, the residuals for the volcanic specimens increase, yielding an even greater deviation from the metamorphic specimens.

Thus the present data agree with the supposition of disorder in volcanic orthopyroxene. Since Virgo and Hafner (1968) have shown that heating above 1000 °C for hours or days causes movement of Fe, the effect of order on the cell dimensions could be tested rigorously by measuring cell dimensions of specimens heated under controlled conditions.

#### *Multivariate best-fit analyses (M. H. H.)*

The conventional multivariate regression analysis used in the previous section assumes that if one parameter (e.g.  $a$ ) is expressed in terms of other parameters

TABLE IV. *Contents of M sites (atomic fractions) and cell dimensions (Å) from the literature*

	Mg	Ca	Al	<i>a</i>	<i>b</i>	Ref.
<i>Specimens from a meteorite and from plutonic and metamorphic rocks</i>						
Shallowater	0.989	0.005	0.000	18.230	8.815	1
37393	0.931	0.003	0.009	18.225	8.828	2
W26	0.922	0.004	0.019	18.239	8.823	1
RF1	0.858	0.019	0.079	18.250	8.812	1
RF1*	0.871	0.005	0.079			
7666	0.836	0.027	0.033	18.251	8.834	1
7666*	0.856	0.005	0.033			
EB38	0.724	0.022	0.033	18.273	8.856	1
EB38*	0.736	0.006	0.033			
EB130	0.692	0.035	0.035	18.284	8.870	1
EB130*	0.712	0.007	0.035			
37096	0.678	0.000	0.128	18.256	8.821	2
344	0.672	0.019	0.082	18.281	8.852	2
6-82-B	0.593	0.033	0.121	18.279	8.847	2
EB41	0.560	0.102	0.036	18.293	8.887	1
EB41*	0.613	0.007	0.035			
37218	0.442	0.024	0.050	18.317	8.924	2
K9	0.383	0.015	0.009	18.353	8.954	1
Klein	0.198	0.006	0.003	18.385	9.020	3
XYZ	0.130	0.019	0.009	18.395	9.027	2
K11	0.117	0.017	0.006	18.404	9.038	2
<i>Specimens from volcanic rocks</i>						
2	0.815	0.034	0.019	18.281	8.853	4
Al-Hy	0.690	0.029	0.147	18.300	8.807	1
5	0.646	0.052	0.011	18.333	8.885	4
6	0.638	0.041	0.065	18.320	8.884	4
7	0.640	0.028	0.053	18.326	8.881	4
8	0.645	0.024	0.031	18.314	8.884	4
10	0.644	0.014	0.020	18.309	8.890	4
11	0.643	0.016	0.009	18.302	8.885	4
13	0.591	0.031	0.038	18.340	8.893	4
14	0.532	0.026	0.009	18.337	8.920	4
DOM 1	0.507	0.032	0.024	18.333	—	1
15	0.471	0.035	0.069	18.334	8.933	4
<i>Synthetic</i>						
Fs	0.000	0.000	0.000	18.42	9.068	5

\* Composition postulated by omission of augite lamellae.

References: 1, Hess, 1952; 2, Ramberg and DeVore, 1951 (cell dimensions obtained from the 14.5.0 reflection in conjunction with values estimated individually from 12.0.0 and 060); 3, Klein, 1966; 4, Kuno, 1954; 5, Akimoto *et al.*, 1965.

(e.g. Mg, Al, and Ca), there is no error in the latter, and that the minimized sum of squares of the residuals depends solely on the former. Such an analysis is correct for the estimation of cell dimensions from diffraction angles for which the parameters *h, k, l* are precisely known to be integers. It is not correct when all parameters have errors. A full statistical analysis would involve consideration of the relative magnitude of the

errors in the separate variables and the interrelation between the errors. In the present example, the cell dimensions  $a$ ,  $b$ ,  $c$  of a particular sample suffer both random errors (e.g. from statistical counting error in the diffraction peaks from the orthopyroxene) and systematic errors (e.g. calibration of the diffraction angles by the standard). The former are uncorrelated but the latter are correlated. The chemical variables also suffer both random and systematic errors, which may be correlated or uncorrelated depending on the details of the analytical procedure and on the subsequent recalculation. It is quite impractical to evaluate the details of all these effects, even if all the sources of error had been detected. However, it is possible to consider simultaneously the errors in all the variables if these errors are assumed to be independent and symmetrically distributed. The mathematical theory is described elsewhere (Hey, 1969).

Because of the considerations given in the preceding paragraphs it was decided to carry out the analysis on the basis of two solid-solution series from Mg 1.0–0.5 and 0.5–0.0. In addition analysis was made using average and minimum Ca. Because of the high Ca content of specimen Y29, and the difficulty of measuring the Ca content even by microprobe analysis, calculations were also made with this specimen omitted. For convenience the calculations are labelled as follows:

A	Mg 1.0–0.5,	Ca average,	Y29 included;	18 specimens
B	Mg 1.0–0.5,	Ca average,	Y29 excluded;	17 specimens
C	Mg 1.0–0.5,	Ca minimum,	Y29 included;	18 specimens
D	Mg 1.0–0.5,	Ca minimum,	Y29 excluded;	17 specimens
E	Mg 0.5–0.0,	Ca average,	14 specimens	
F	Mg 0.5–0.0,	Ca minimum,	14 specimens	

In the calculations, equal weight was given to each specimen even though the errors for the cell dimensions vary considerably. Because there are so few data, use of weights would result in some coefficients being determined principally by only one or two data. Calculations were made in double-length arithmetic on the Atlas computer at the University of London; hence computational errors can be ignored.

In order to obtain the best fit, the probable errors of the data were estimated from knowledge of the experimental microprobe and X-ray techniques to be  $\epsilon_{Fe}$  0.01,  $\epsilon_{Mg}$  0.01,  $\epsilon_{Ca}$  0.003,  $\epsilon_{Al}$  0.005,  $\epsilon_a$  0.003,  $\epsilon_b$  0.0015,  $\epsilon_c$  0.002. The data were normalized,  $\xi_{Mg} = (Mg - \bar{Mg})/\epsilon_{Mg}$  *et sim.*, and the best-fitting 3-flat in 7-dimensional space calculated. It is specified by four mutually orthogonal equations (cited with normalized coefficients;  $\Sigma \alpha^2 = 1$ ), and these are the four latent vectors corresponding to the four smallest latent roots of the matrix of squares and products of the normalized data (Hey, 1969).

Since the chemical data are related by the exact equation  $Fe + Mg + Ca + Al = 1$ , the best fitting prime<sup>1</sup> is the standardized form of this relation, and has zero coefficients in the physical variables and a zero or near-zero latent root. The other three latent vectors have non-zero coefficients in all 7 variables, and so are of little practical

<sup>1</sup> In  $n$ -dimensional geometry a linear surface of  $n-1$  dimensions, corresponding to a plane in 3-space, is called a prime; a linear surface of  $r$  dimensions is called an  $r$ -flat; 2- and 1-dimensional surfaces retain their usual names of plane and line.

use as they stand; however, just as a line in 3-space may be defined by any two planes intersecting in it, and any linear combination of the equations of these lines will also be a plane containing the same line, so in 7-space any linear combination of the four best-fitting primes yields a fully consistent relation; and this enables us to eliminate any three variables to produce an equation in the other four. It is, however, necessary to exercise some caution in selecting sets of four variables for an equation; and for this reason the programme is arranged to give also a product-moment correlation matrix, which shows which pairs of variables are most closely related. If any pair of variables that are strongly correlated appear on the right-hand side of an equation of form  $y = px + qy + rz + \dots$ , the coefficients of those variables will carry very large standard errors—it will be possible to alter one of them considerably without seriously affecting the accuracy of the equation as a measure of  $y$  provided the other is also altered suitably.

The correlation matrices for sets A and B are:

A:	Fe	Mg	Ca	Al	<i>a</i>	<i>b</i>	<i>c</i>
	1	-0.956	0.012	0.212	0.907	0.834	0.972
		1	-0.038	-0.484	-0.851	-0.647	-0.916
			1	-0.115	0.344	0.135	0.128
				1	0.073	-0.345	0.259
					1	0.849	0.919
						1	0.796
							1
B:	Fe	Mg	Ca	Al	<i>a</i>	<i>b</i>	<i>c</i>
	1	-0.955	0.581	0.201	0.953	0.833	0.978
		1	-0.501	-0.481	-0.879	-0.637	-0.952
			1	-0.120	0.687	0.621	0.585
				1	0.077	-0.360	0.252
					1	0.866	0.936
						1	0.792
							1

The matrices for sets C and D do not differ much from those for sets A and B, while the matrices for the two sets with  $Mg < 0.5$ , E and F, only differ in showing a much stronger correlation of Al with Fe, Mg, and the physical variables. It will be evident from these matrices that the only equations likely to be stable are those relating one of the physical variables, Ca, Al, and either Fe or Mg; it will also be evident from the very weak correlation between Al and *a* in sets A to D that an equation for *a* in terms of the composition is likely to show either a very small coefficient for Al or a coefficient with a large standard error; in sets E and F, with  $Mg < 0.5$ , the physical variables are well correlated with Al, but the correlation of *a* and *b* with Ca is very weak.

The very strong correlation of Fe and Mg is, of course, simply the consequence of the short range of Ca and moderate range of Al; but the appreciable inverse correlation of Al and Mg in sets A to D and the fairly strong positive correlation of Ca and Fe in sets B and D with specimen Y29 excluded (a correlation that vanishes when Y29 is included), while no doubt partly an accidental consequence of the selection of

specimens, probably also result in part from geochemical coherence of elements selected by orthopyroxene during growth. It is notable that in sets E and F the negative correlation of Al and Mg becomes positive.

The standardized form of the equation  $Fe + Mg + Ca + Al = 1$  is  $10\xi_{Fe}/3\sqrt{26} + 10\xi_{Mg}/3\sqrt{26} + \xi_{Ca}/\sqrt{26} + 5\xi_{Al}/3\sqrt{26} = 0$ , and this is the equation of the latent vector corresponding to the zero latent root in the latent vector expression of the best-fitting

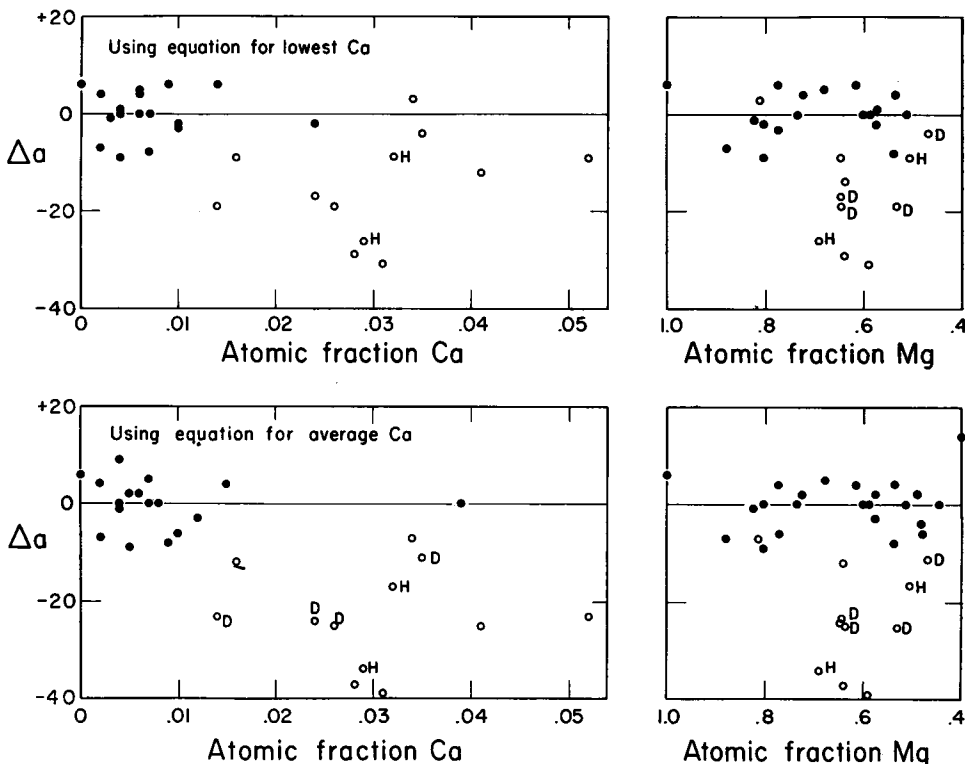


FIG. 3. Residuals of the regression equations for  $a$  for the specimens of table II (●), compared with those for volcanic specimens studied by Hess (1952) and by Kuno (1954) (○).

3-flat for all six sets of data; the equations of the other three vectors and the corresponding latent roots are listed in table V.

Since the latent vectors are orthogonal primes, summing the latent roots for the cited vectors yields the sum of squared residuals to the best-fitting 3-flat,  $\Sigma\lambda$ . The root-mean-square standardized residual is then  $\bar{R} = \sqrt{(7\Sigma\lambda/4N)}$ , where  $N$  is the number of sets of related data (18, 17, or 14). If the relations were all truly linear, the observations reasonably numerous, and the assessments of experimental error accurate,  $\bar{R}$  should approximate to unity. As will be seen from table V,  $R$  is high, but not excessively so for the relatively small values of  $N$ ; it is, however, large enough to suggest that the relations are not strictly linear.



However, plots of the individual residuals to the 3-flat against each variable do not yield any visual evidence of non-linearity, and although the number of points is rather small, it seems likely that an underassessment of the probable experimental errors is

TABLE V. Latent vectors defining the best-fitting 3-flat to the standardized orthopyroxene analyses and cell-dimensions, sets A-F (as defined in the text); with each set of three vectors,  $10\xi_{\text{Fe}}/3\sqrt{26} + 10\xi_{\text{Mg}}/3\sqrt{26} + \xi_{\text{Ca}}/\sqrt{26} + 5\xi_{\text{Al}}/3\sqrt{26} = 0$  must be included as fourth. The vectors are presented as the coefficients of  $P\xi_{\text{Fe}} + Q\xi_{\text{Mg}} + S\xi_{\text{Ca}} + T\xi_{\text{Al}} + U\xi_a + V\xi_b + W\xi_c = 0$ , and the corresponding latent roots,  $\lambda$ , are included. For each set, the root-mean-square standardized residual,  $\bar{R}$ , is also cited. The mean values, from which the  $\xi$  are measured, are also given

P	Q	S	T	U	V	W	$\lambda$	$\bar{R}$	Set
0.1638	0.0560	-0.4444	-0.1730	0.7550	-0.2251	-0.3491	26.61	2.53	A
0.4699	-0.2603	0.3207	-0.6116	-0.2228	-0.4036	-0.1481	21.78		
-0.0343	-0.1526	0.2082	0.2488	-0.1381	0.2492	-0.8883	16.79		
0.5147	-0.2314	0.0594	-0.6020	0.0293	-0.4259	-0.3652	22.34	2.29	B
-0.0435	-0.0375	-0.2496	0.3120	0.1467	0.2469	-0.8686	18.07		
0.1345	0.1685	-0.8850	-0.0749	0.3104	-0.1232	0.2308	10.86		
0.4921	-0.2565	0.2432	-0.6171	-0.1151	-0.4186	-0.2522	22.81	2.36	C
0.0955	0.0128	-0.4845	0.0741	0.4912	0.0086	-0.7136	20.42		
0.1468	0.1600	-0.5580	-0.2788	0.3387	-0.2944	0.6020	14.84		
-0.4985	0.2494	-0.1905	0.6126	0.0445	0.4237	0.3102	22.51	2.21	D
0.0106	-0.0566	-0.2659	0.2515	0.1445	0.2025	-0.8949	18.15		
0.2045	0.1371	-0.8726	-0.1597	0.2725	-0.1841	0.2104	11.89		
-0.2343	0.2534	-0.2329	0.1015	0.6142	0.0505	-0.6606	40.70	2.94	E
0.4310	-0.0319	-0.4452	-0.5310	0.3605	-0.3961	0.2151	22.69		
0.2779	-0.3275	0.6549	-0.2938	0.0340	-0.2474	-0.4877	5.65		
-0.2632	0.2320	-0.1335	0.1425	0.5093	0.1040	-0.7540	39.69	2.89	F
0.4213	-0.0086	-0.4811	-0.5368	0.3923	-0.3830	0.0461	22.95		
0.2646	-0.3434	0.7200	-0.2744	0.0219	-0.2464	-0.3965	3.95		

Mean values (unstandardized)

$\bar{\text{Fe}}$	$\bar{\text{Mg}}$	$\bar{\text{Ca}}$	$\bar{\text{Al}}$	$\bar{a}$	$\bar{b}$	$\bar{c}$	Set
0.2414	0.6975	0.0084	0.0527	18.2702	8.8497	5.2013	A
0.2488	0.6912	0.0066	0.0534	18.2700	8.8506	5.2017	B
0.2434	0.6971	0.0069	0.0526	18.2702	8.8497	5.2013	C
0.2495	0.6912	0.0059	0.0534	18.2700	8.8506	5.2017	D
0.6447	0.3198	0.0146	0.0209	18.3584	8.9679	5.2320	E
0.6469	0.3198	0.0124	0.0209	18.3584	8.9679	5.2320	F

responsible for at least part of the excess of  $\bar{R}$  over unity. The difference between  $\bar{R}$  for the four sets A to D is too marginal to indicate any superiority of one set; nor is the difference of  $\bar{R}$  between sets E and F enough to decide between them.

By taking appropriate combinations of the four latent vectors, three variables can be eliminated to produce derived vectors all of which are perfectly consistent and pass through the best-fitting 3-flat, and these can then be destandardized. Derived

TABLE VI. *Multivariate best-fit equations for the orthopyroxenes of table II, with their standard errors,  $\hat{\sigma}$ . The standard errors of the coefficients are written under each coefficient. The equations have been derived in the form  $a$  (or  $b$  or  $c$ ) =  $p+q\text{Fe}+r\text{Ca}+s\text{Al}\pm\hat{\sigma}$  =  $p'+q'\text{Mg}+r'\text{Ca}+s'\text{Al}\pm\hat{\sigma}$ . The coefficients  $p'$ ,  $q'$ ,  $r'$ , and  $s'$  are directly comparable with the coefficients of the regression equations in the lower half of table III, but  $\hat{\sigma}$  and  $\sigma$  are not comparable. For the significance of the coefficients in the line 'Comp.', see text*

$p$	$q$	$r$	$s$	$\hat{\sigma}$	$p'$	$q'$	$r'$	$s'$	Set	Range
<i>Equations for a</i>										
18.2305	0.1428	0.859	-0.0377	0.0053	18.3733	-0.1428	0.716	-0.1805	A	} Mg 1-0.5
	107	152	318			107	110	356		
18.2257	0.0995	2.901	0.0056	0.0085	18.3252	-0.0995	2.801	-0.0940	B	
	227	715	530			227	729	643		
18.2286	0.1369	1.425	-0.0301	0.0059	18.3625	-0.1369	1.288	-0.1670	C	
	123	272	359			123	275	406		
18.2245	0.1057	3.215	0.0014	0.0097	18.3301	-0.1057	3.110	-0.1043	D	} Mg 0.5-0
	240	826	599			240	840	710		
18.1604	0.2634	1.647	0.201	0.0086	18.4238	-0.2634	1.384	-0.063	E	
	235	469	189			235	458	172		
18.1415	0.2818	2.263	0.316	0.0091	18.4234	-0.2818	1.981	0.034	F	
	302	684	234			302	667	211		
—	0.186	1.05	-0.7	—	—	—	1.35	—	Comp.	
<i>Equations for b</i>										
8.8164	0.2073	0.208	-0.3526	0.0038	9.0238	-0.2073	0.000	-0.5599	A	} Mg 1-0.5
	77	109	228			77	71	165		
8.8166	0.2090	0.127	-0.3543	0.0039	9.0258	-0.2090	-0.081	-0.5637	B	
	105	330	245			105	337	297		
8.8168	0.2091	0.096	-0.3546	0.0037	9.0259	-0.2901	-0.113	-0.5637	C	
	77	171	226			77	173	256		
8.8169	0.2100	0.048	-0.3554	0.0037	9.0268	-0.2100	-0.162	-0.5654	D	} Mg 0.5-0
	96	330	239			96	335	284		
8.7632	0.3146	0.510	-0.265	0.0044	9.0778	-0.3146	0.195	-0.580	E	
	123	245	99			123	240	90		
8.7599	0.3176	0.620	-0.245	0.0042	9.0772	-0.3176	0.302	-0.563	F	
	124	280	96			124	274	86		
—	0.272	0.22	-0.5	—	—	—	-0.13	—	Comp.	
<i>Equations for c</i>										
5.1773	0.0894	0.179	0.0184	0.0025	5.2667	-0.0894	0.090	-0.0710	A	} Mg 1-0.5
	50	70	147			50	71	165		
5.1773	0.0890	0.192	0.0186	0.0025	5.2663	-0.0890	0.103	-0.0704	B	
	68	215	159			68	219	193		
5.1772	0.0894	0.199	0.0184	0.0025	5.2666	-0.0894	0.110	-0.0709	C	
	51	113	150			52	114	169		
5.1773	0.0897	0.175	0.0180	0.0025	5.2670	-0.0897	0.085	-0.0717	D	} Mg 0.5-0
	64	218	158			64	222	188		
5.1884	0.0477	0.761	0.082	0.0032	5.2361	-0.0477	0.714	0.034	E	
	90	178	72			90	174	65		
5.1830	0.0539	0.953	0.111	0.0036	5.2369	-0.0539	0.899	0.057	F	
	107	242	83			107	236	74		
—	0.059	0.16	≈0	—	—	—	0.07	—	Comp.	

equations for the three cell-dimensions in terms of Fe, Ca, and Al and in terms of Mg, Ca, and Al are given in table VI; though the correlation matrices suggest that no other equations are likely to be sufficiently stable to be of practical interest, equations for the four chemical variables in terms of the cell dimensions are given in table VII.

It should be emphasized that the standard errors of the coefficients are not independent. They imply that 'nearly as good' a fit to the data could be obtained with this coefficient altered by this much *provided the other coefficients were adjusted accordingly*; 'nearly as good' means within the average squared residual.

It should be emphasized also that the cited r.m.s. residuals of the equations, quoted on the right, refer to the present set of data only. They are, however, a guide to the

TABLE VII. *Further multivariate best-fit equations for the orthopyroxenes of table II. The equations for each of the six sets of data are strictly consistent with the equations for the same set in table VI. The equations are given in the form*  

$$\text{Fe (or Mg or Al or Ca)} = P + Qa + Rb + Sc \pm \hat{\sigma}$$

P	Q	R	S	$\hat{\sigma}$	Set	P	Q	R	S	$\hat{\sigma}$	Set
<i>Equations for Fe</i>											
-23.478	-3.119	1.051	13.728	0.035	A	-47.140	-0.736	0.554	10.752	0.028	B
	1.364	634	1.983				1.254	522	1.718		
-37.495	-1.737	0.774	12.040	0.031	C	-48.848	-0.585	0.534	10.585	0.027	D
	1.140	532	1.657				1.230	512	1.688		
-40.514	5.539	0.399	-12.252	0.059	E	-33.603	4.999	0.818	-12.398	0.058	F
	2.656	1.850	4.298				2.628	1.830	4.253		
<i>Equations for Mg</i>											
40.723	2.340	1.610	-18.656	0.045	A	57.395	0.666	1.961	-16.578	0.040	B
	1.674	781	2.434				1.811	754	2.483		
47.416	1.677	1.750	-17.850	0.042	C	58.508	0.555	1.984	-16.441	0.040	D
	1.582	737	2.299				1.796	748	2.462		
62.952	-9.552	2.098	17.951	0.089	E	49.552	-8.644	1.366	18.579	0.088	F
	4.028	2.805	6.517				3.967	2.763	6.420		
<i>Equations for Al</i>											
1.027	0.866	-2.383	6.908	0.017	A	-4.599	-0.301	-2.501	6.206	0.016	B
	645	301	948				721	300	988		
0.261	-0.792	-2.398	6.823	0.017	C	-4.599	-0.301	-2.501	6.206	0.016	D
	637	297	926				721	300	989		
-19.238	4.888	-2.770	-8.722	0.042	E	-12.921	4.446	-2.421	-8.979	0.041	F
	1.891	1.323	3.060				1.848	1.287	2.990		
<i>Equations for Ca</i>											
-17.273	1.645	-0.279	-1.979	0.010	A	-4.656	0.371	-0.014	-0.381	0.003	B
	352	164	511				142	59	195		
-9.183	0.852	-0.125	-1.013	0.005	C	-4.061	0.330	-0.016	-0.351	0.003	D
	195	91	283				113	59	196		
-2.201	-0.874	0.274	3.022	0.011	E	-2.028	-0.802	0.236	-2.798	0.010	F
	817	571	1.319				784	546	1.270		

accuracy of any prediction based on the equation provided that the new observations have comparable accuracy to the present observations, and fall within the same ranges. Extrapolation of the equations may be inaccurate especially for the short-range variables Ca and Al. A further condition is that the new data must be taken for orthopyroxenes with the same crystal structure, and must not suffer systematic observational errors with respect to the present data. Thus the equations must not be used for volcanic orthopyroxene unless verified by actual measurements.

Finally it should be emphasized that there are some pitfalls in the interpretation of the modified equations. In each equation for a cell dimension expressed in terms of chemical variables, one chemical variable has necessarily been eliminated, and the coefficients refer to replacement of the eliminated variable by those left in: thus in

table VI,  $a = 18.230 + 0.143 \text{ Fe} - 0.038 \text{ Al} + 0.86 \text{ Ca}$  exhibits the effects of the replacements Fe for Mg, Al for Mg (more accurately, AlAl for MgSi), and Ca for Mg. Since the coefficient 0.038 has a standard error of 0.032 it is not significant, which means that Al has essentially the same effect as Mg on  $a$ . In the equations for  $a$  in terms of Mg, Al, and Ca, this conclusion is obvious since the coefficients for Mg and Al ( $-0.143 \pm 0.011$  and  $-0.180 \pm 0.036$ ) are not significantly different. Because of the strong correlation of Fe and Mg in these data, no equations involving both Fe and Mg have been computed since they would be very unstable. The appreciable correlation of Mg and Al shown earlier in the correlation matrices for all four sets of calculations weakens the evidence for equivalence of Mg and Al. Similarly the correlation of Mg and Ca, apparent in sets B and D only, makes it difficult to recognize whether the substitution  $\text{Mg} \rightleftharpoons \text{Ca}$  affects the cell dimensions, so far as these sets of data are concerned.

*Interpretation of the results in crystal-chemical terms (M. H. H., R. A. H., J. V. S.)*

In this section the coefficients will be examined first for their statistical significance and then in terms of expected changes using the simple electrostatic hard-sphere model. Although the ionic model is too simple, it is not possible to estimate covalent contributions except in a very elementary manner. Magnetic interactions can be expected, especially for Fe-rich samples, but again it is difficult to estimate their influence.

Interpretation will be based on the assumption that the minor elements are dispersed throughout the crystal structure, and do not cluster together to form incipient nuclei. In addition it will be assumed that there are no local co-operative substitutions to minimize local strain. For example, Al might substitute for Mg in  $M_1$  adjacent to Ca substituting for Fe in  $M_2$ ; such a spatially coupled substitution on adjacent sites should be favoured energetically over a spatially random distribution. Finally it should be noted that the present mathematical analysis, using linear first-order terms, implies that each substitution effects changes in cell dimensions independently of the other atoms. This assumption is probably wrong—e.g. the effect of Al substituting for Mg in  $M_1$  probably depends on the kind of atoms occupying the  $M_2$  sites.

The crystal structure of pyroxene consists of  $\text{SiO}_3$  chains of tetrahedra bonded to slabs of edge-sharing octahedra. Many papers give descriptions of the crystal structure, which may be assembled in the following steps: place on a flat surface one chain of tetrahedra parallel to  $c$  with oxygen apices pointing upwards. Slide another chain parallel to it with the oxygen apices pointing down and adjust it so that the side oxygens partly nestle between the side oxygens of the first chain. Repeat the alternation to produce a slab of interlocked chains in the  $bc$  plane. The surface of the layer provides dimples between groups of three oxygens nearly in an equilateral triangle, composed of two apical oxygens of one chain and one basal oxygen of another chain; place an  $M_1$  cation on each alternate possible dimple parallel to  $c$ . The surface also provides larger dimples between five oxygens, composed of one apical oxygen of one chain and four basal dimples of the other chain; place  $M_2$  cations in each dimple and move as far as possible away from the  $M_1$  cations by distorting the nearby oxygens. Place another slab of chains over the first slab. Finally, choose the positions of  $M_1$  and  $M_2$  cations

on top of the second slab according to the polymorph required. For clinopyroxene, the  $M$  cations are related in projection on the  $bc$  plane by a vector which always goes in the same direction along  $c$ . For orthopyroxene the vector goes twice along  $+c$  and then twice along  $-c$ . The  $M_1$  polyhedron is fairly close to a regular octahedron, but the  $M_2$  polyhedron is rather distorted and larger; its coordination is irregular with 6–8 near neighbours. The  $\text{SiO}_3$  chain is kinked and capable of adjustment in response to changes in the octahedra. Small cations, which prefer regular octahedral coordination, should go into  $M_1$ , while large cations, which tolerate irregular coordination, should prefer  $M_2$ . Details of the polymorphism and coordination of pyroxenes with compositions principally in the Di–Hd–Fs–En quadrilateral are given in many places (Brown, Morimoto, and Smith, 1961; Burnham, 1967; Ghose, 1965; Lindemann, 1961; Morimoto, Appleman, and Evans, 1960; Morimoto and Koto, 1968).

Direct comparison of the cell dimensions of natural orthopyroxenes with synthetic ones is hampered by the paucity of data for the latter. Apart from accurate cell dimensions for enstatite and orthoferrosilite, there are data only for the substitution of  $\text{AlAl}$  for  $\text{MgSi}$  in ortho-enstatite by Skinner and Boyd (1964).

If the contention of Ito (1935, 1950) is correct in that the crystal structure of an orthopyroxene is merely that of a chemically identical clinopyroxene twinned on a unit cell scale, the observed changes in cell dimensions of clinopyroxenes should be directly applicable to changes in orthopyroxenes. Comparisons of the crystal structures of ortho- and clino-ferrosilite by Burnham (1967) and of ortho- and clino-enstatite by Morimoto and Koto (1968) show that Ito's hypothesis is obeyed fairly well. However, the different thermodynamic stabilities show that this hypothesis is not strictly true, and some differences must exist. Perhaps the differences are rather more marked in the effect of minor elements on the structure.

Some pertinent data on clinopyroxenes are cell dimensions for synthetic diopside with many types of substituent minor elements (Coleman, 1962) and cell dimensions for synthetic diopside–acmite solid solutions (Nolan and Edgar, 1963). Data on the cell dimensions of natural, chemically analysed clinopyroxenes (Di–Hd–En–Fs quadrilateral) are given by Kuno and Hess (1953), Brown (1960), and Viswanathan (1966).

In comparing cell dimensions of ortho and clino forms of pyroxene, if Ito's hypothesis were exactly obeyed:  $2a \sin \beta$  (clino) =  $a$  (ortho),  $b$  (clino) =  $b$  (ortho),  $c$  (clino) =  $c$  (ortho).

The most pronounced substitution in orthopyroxenes is Fe for Mg. The coefficients taken from column  $q$  of table VI show the effect of complete replacement of all the Mg by Fe even though each best fit was made only for half the compositional range. It will be seen that for the range Mg 1 to 0.5, the expansions in  $b$  and  $c$  are essentially unaffected by the choice of data, but the expansion in  $a$  is slightly affected by the choice of average or minimum Ca, and strongly affected by the omission of the Y29 data. The expansions for the range Mg 0.5 to 0 are slightly affected by choice of average or minimum Ca. For comparison, the differences between the cell dimensions of clino-enstatite and clinoferrosilite are given in column  $q$ , in the lines 'Comp.'.

In spite of the effects caused by the choice of data, there is no doubt that the substitution of Fe for Mg in these metamorphic samples causes quite different changes in cell dimensions in Mg-rich from those in Fe-rich compositions. From the

Mössbauer and X-ray diffraction data quoted in the introduction, these differences can be ascribed to the different environments of the  $M_1$  and  $M_2$  sites.

For detailed interpretation it is probably better to look at the proportional expansions expressed as  $\Delta a/a$ , etc. These are:

	Mean sets			Mean
	Sets A-D	Sets E-F	A-F	Cl-en-Cl-fs
In $a$	0.5-0.8 %	1.4-1.5 %	1.0 %	1.0 %
In $b$	2.3 %	3.5 %	2.9 %	3.1 %
In $c$	1.7 %	0.9-1.0 %	1.3 %	1.1 %

The mean expansions for the ortho are close to those for the clino series, and this makes it likely that the cell dimensions of the clino series can be predicted from knowledge of those for the ortho: however, the possible change in site preference must be taken into account since those clino specimens measured so far come principally from volcanic rocks. The cell dimensions  $a$  and  $b$  of volcanic orthopyroxenes seem to be larger than those of metamorphic specimens (table IV): this expansion could be partly the result of the usual expansion found for disordered crystals, but partly the result of the greater effect of Fe substitution in  $M_1$  as shown by the above data. The latter should cause a reduction in  $c$  compared with metamorphic specimens.

For the present data, Fe is principally replacing Mg in  $M_2$  in the range Mg 1.0-0.5 and in  $M_1$  for the range Mg 0.5-0. The smaller change of  $(\Delta a + \Delta b + \Delta c)$  in  $M_2$  than in  $M_1$  can be explained by the greater irregularity of coordination of the former. The resulting adjustment of oxygen atoms around  $M_2$  consists partly of a general expansion in all directions, and partly of a shear of one chain of tetrahedra sliding parallel to  $c$  with respect to the other. The octahedron around  $M_1$  is more regular and the general expansion is forced to be greater: here the principal expansion consists of the chains being forced apart along the  $b$  axis with the shear between the chains relatively smaller because of the near-interlocking of two apical oxygens of one chain with a basal oxygen of the next chain. The detailed effects are more complex than those given here, but the major effects are the ones described.

Since Al is a rather short-range variable, the effects of its substitution for Mg (or rather, of AlAl for MgSi) cannot be assessed very accurately (table VI, column  $s$ ); in this column, in the lines 'Comp.', the effect of substitution of AlAl for MgSi in synthetic enstatite found by Skinner and Boyd (1964) are included, recalculated by a linear proportion from the maximum observed content of 15 wt %  $\text{Al}_2\text{O}_3$  to complete substitution of Mg by Al (and automatically of Si by Al). The choice of data has a marked effect on the coefficients for the natural orthopyroxenes. In Mg-rich compositions, the substitution of Al for Mg apparently has little effect on  $a$  and  $c$ , but causes a significant decrease in  $b$ . In Fe-rich compositions, the substitution of Al for Mg apparently causes an increase in  $a$  and  $c$  (but hardly significant) and a significant decrease in  $b$ . The present results do not appear to agree with those for the synthetic substituted enstatites for which major decreases in  $a$  and  $b$  were found. The difference presumably results partly from interaction between cations in the  $M_1$  and  $M_2$  sites. In the natural specimens, Al probably enters the  $M_1$  site replacing Mg. The data for sets

E and F show smaller contractions (indeed  $a$  and  $c$  actually increase) as a result of Al substitution than do the data for sets A to D. Thus it appears that substitution of Al for Mg causes greater contraction in Mg-rich specimens than in Fe-rich ones. Extrapolating to enstatite would result in greater contractions than those shown for sets A to D. However, reasonable extrapolations still do not give values as great as those found for the coefficients of  $a$  and  $b$  in synthetic specimens. Two further effects may contribute: in the synthetic enstatites, Al may replace Mg in both  $M_1$  and  $M_2$ ; in natural orthopyroxenes the Al content in the  $M$  and Si sites tends to be unbalanced because of the presence of ferric iron (fig. 1). Detailed crystal-structure analysis of synthetic Al-rich enstatites, and measurement of cell dimensions for synthetic orthopyroxenes containing known amounts of Al and both ferrous and ferric iron would be needed to fully resolve these suggestions.

Calcium should occupy the larger  $M_2$  site. Unfortunately its small range in this suite of metamorphic orthopyroxenes and the uncertainty of the microprobe analyses causes difficulty in evaluating the coefficients. The coefficients in column  $r$  of table VI show the effect of replacing Mg by Ca at constant Fe, and may be compared with the effect found in the clinopyroxenes: the figures in column  $r$  under 'Comp.' are double the difference in cell dimensions  $a \sin \beta$ ,  $b$ , and  $c$  between synthetic diopside (Nolan and Edgar, 1963) and clinoenstatite (Stephenson *et al.*, 1966). In column  $r'$  of table VI, the coefficients show the effect of replacing Fe by Ca at constant Mg, and may be compared ('Comp.') with double the difference between  $a \sin \beta$ ,  $b$ , and  $c$  of synthetic clinoferrosilite (Burnham, 1965) and a natural hedenbergite (no. 8 of Viswanathan, 1966). The agreement between the coefficients for sets A and C with Ca replacing Mg, on the one hand, and the coefficients calculated for the substitution of Ca in clinoenstatite to yield diopside is remarkably good. Indeed one might claim that this agreement shows that the true Ca content is that obtained by including Y29 even though microprobe analysis was particularly difficult for this specimen. For Fe-rich orthopyroxenes, the substitution of Ca for Fe at constant Mg content is the substitution of Ca for Fe in  $M_2$ : thus the coefficients should be similar to those calculated by comparing clinoferrosilite with hedenbergite. The coefficients for  $a$  (sets E, F) agree quite well, but those for  $b$  differ by more than one standard error, and those for  $c$  by over three times the error. If the Ca is going partly into  $M_1$  in Fe-rich orthopyroxenes these discrepancies might be resolved, since not only would the cell volume tend to increase because of disorder, but the cell dimensions (especially  $c$ ) would be forced to increase more as a result of the lower tolerance of the oxygens around the regular  $M_1$  site to adjust for a larger cation (cf. discussion for Mg,Fe substitution). Perhaps Mössbauer data will give indirect evidence on the distribution of Ca between the  $M_2$  and  $M_1$  sites.

Finally it appears that for all orthopyroxenes:  $a$  is increased by Fe, is affected little by Al, and markedly increased by Ca;  $b$  is increased by Fe, strongly decreased by Al, and hardly affected by Ca;  $c$  is increased by Fe, hardly affected by Al, and probably increased by Ca. The coefficients differ markedly for some substitutions as the pyroxene goes from Mg-rich to Fe-rich compositions. The marked increase of  $a$  by Ca and decrease of  $b$  by Al has already been noted by Kuno (1954) and Howie (1963).

In theory, the contents of Mg, Al, and Ca could all be estimated from measurement of  $a$ ,  $b$ , and  $c$ . In practice it seems certain that different equations must be used for pyroxenes from different geologic environments, and even when the equations for the correct environment have been used, the errors quoted in table VII show that the resulting estimates of Mg, Al, and Ca have low accuracy. For Ca, the value obtained would depend greatly on the set of equations used for the interpretation. Leake (1968) has found a standard error of 0.05 mg for regression of  $\gamma$  against mg, and suggests that since some of the error results from poor chemical analysis mg could be determined optically to 0.03 providing that the pyroxene is not abnormal in minor constituents. Perhaps the optical properties will need re-examination in the light of recent data on variable site preference; perhaps we are unduly pessimistic but it seems doubtful that the Mg, Al, and Ca contents can be estimated from physical properties of orthopyroxene to an accuracy better than about 0.04, 0.02, and 0.01 (where cations in  $M$  sites total to unity). These values may be useful in routine petrography, but electron microprobe analysis can give a higher accuracy for these elements and for other minor elements unless sub-microscopic lamellae cannot be distinguished by the focused electron beam.

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