

*Cell dimensions of olivine*

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*Summary.* Cell dimensions obtained from X-ray powder photographs of twenty-four natural olivines and one synthetic forsterite have been related to the cation contents by a new statistical procedure developed by M. H. Hey. Unlike conventional statistical analysis, which assumes error only in one parameter, this procedure simultaneously considers the estimated errors in all variables.

Linear terms in Ca, Mn, Mg (or  $\text{Fe} \equiv 1 - \text{Mg} - \text{Ca} - \text{Mn}$ ) satisfactorily account for the cell dimensions, and there was no need to invoke a term in  $\text{Mg}^2$ . Since there are three cell dimensions and three chemical unknowns, it is theoretically possible to estimate the major cations in olivine just from the cell dimensions. However, the coefficients for Mn and Fe are so similar and the ranges of Ca and Mn are so small that the technique would be impractical.

Data for ideal (Mg,Fe) olivines were estimated by adjusting the cell dimensions by linear extrapolation from the cell dimensions of tephroite and monticellite. A simple chemical term was sufficient to account for each cell dimension. The linear relation between cell volume and Mg is consistent with the complete disorder of Mg and Fe revealed by parallel single-crystal X-ray studies.

The cell dimensions of a synthetic fayalite deviate significantly from those of natural fayalites after correction for the effects of Ca and Mn substitution in the latter: some structural or chemical difference, probably involving ferric iron, is indicated.

No superstructure lines have been found, in contradiction to Eliséev's data.

THE present measurements on the cell dimensions of olivine were made as part of a programme to determine whether the Mg and Fe atoms in olivine are disordered, and whether olivine approaches an ideal solid solution. Sahama and Torgeson (1949) and Bloss (1952) concluded that heats of solutions and densities of olivine were consistent with ideal substitution. Yoder and Sahama (1957) from a plot of the spacings of the 130 planes with chemical composition for natural olivines suggested that the variation of cell parameters did not differ greatly from Vegard's rule, though Jambor and C. H. Smith (1964) reported that there is 'a relatively sharp break' from a linear relation of spacing versus composition, and suggested that 'the curvature in the determinative data is probably related at least in part to ordered substitution' of Fe for Mg. Agterburg (1964) made a more extensive statistical analysis.

Henriques (1957) gave equations for relating the cell dimensions of natural olivine to the Mg, Mn, and Fe contents. Smith and Strenstrom (1965) and Smith (1966) have shown that when allowance is made for errors in chemical analysis and for lattice expansion by Ca and Mn, there is a continuous, almost linear, relation between  $d_{130}$  and atomic % Mg in natural olivines. Fisher (1967) has given preliminary cell dimensions of synthetic olivines that show a linear variation of  $b$  and  $d_{130}$  with Mg content, but a slight systematic curvature of  $a$ ,  $c$ , and  $V$ .

Nafziger and Muan (1967) found that  $d_{131}$  and  $d_{112}$  varied linearly across the olivine samples crystallized in the synthetic  $\text{MgO}-\text{FeO}-\text{SiO}_2$  system at 1200 °C and  $10^{-12}$  atm. of oxygen pressure. However, they found a moderate positive deviation of the activities of the Fo and Fa molecules. Lehmann, Dutz, and Koltermann (1961) and Duke and Stephens (1964) have shown that the absorption frequencies of infra-red radiation are linearly related to Fe. Gibbs, Moore, and Smith (1964) and Birle, Gibbs, Moore, and Smith (1968) have shown from X-ray diffraction estimates of electron density that the Mg and Fe atoms of two hortonolites, one from a volcanic and one from a plutonic environment, are equally distributed between the two possible sites: thus there seems no need to invoke the suggestion of Ghose (1962) that the larger  $\text{Fe}^{2+}$  cations would concentrate into the  $M_2$  site.

Contradicting the above evidence for ideal or near-ideal substitution in olivine is the study of Eliséev (1957) who estimated optically the Mg:Fe ratios of several olivines and claimed that the measured cell volumes deviated greatly from Vegard's rule. He also observed extra reflections in the powder patterns claimed to be the result of 'secondary diffraction' in a unit cell with doubled  $c$ .

*Experimental.* Twenty-six of the samples used as tests of microprobe analytical techniques (Smith, 1966) were found suitable for determination of cell dimensions by X-ray powder methods. Two X-ray patterns were made for each sample, one of olivine, and one containing added spinel as an internal standard. Initially, pairs of patterns were made of three samples using a diffractometer, a Guinier camera and a 114.6 mm Buerger-type camera. Clear resolution of high-angle lines and ease of sample preparation resulted in choice of the latter instrument. Filtered  $\text{Fe-K}\alpha$  radiation was used throughout. To minimize absorption, sample spindles were diluted with Duco cement and held to a diameter of 0.15 mm. Each pattern was measured thrice over several weeks with a reproducibility near 0.001 cm. After averaging, the measurements were corrected using the known positions of the lines from the spinel standard,

which had previously been compared with a Spec-pure silicon standard assumed to have  $a$  5.43064 Å. The olivine lines were indexed with the aid of intensities estimated from single-crystal patterns. Lines from pyroxene and spinel impurities in some samples were avoided. Of the 60 or so lines measured for each pattern about 20–30 were especially suitable for estimation of the cell parameters using least squares techniques (Smith, 1956; Burnham, 1962). Comparison of results from selected high-angle and low-angle lines with those for the whole data showed no systematic discrepancies. The values given in table I are for the most suitable lines selected from the entire pattern.  $\lambda(\text{Fe-}K\alpha) = 1.93728$  Å was used for  $2\theta$  less than  $82^\circ$  and  $\lambda(\text{Fe-}K\alpha_1) = 1.93597$  Å for higher angles. Some specimens gave broad lines indicating chemical zoning: for these the error is greater than average.

#### *General discussion on statistical analysis*

Regression analyses were carried out between the chemical parameters and the cell dimensions. Unfortunately the proportional errors in the chemical parameters are in about the same range as the proportional errors in the cell dimensions. Thus the Mg values are likely to be in error by 1–2 % of the total range of 100 % (and perhaps larger for the chemically zoned specimens). The proportional errors of  $a$ ,  $b$ ,  $c$ , and  $V$  run about 2, 0.5, 0.5, and 0.5 % of the total ranges from forsterite to fayalite. The standard technique of least-squares regression analysis (see, e.g., Hey, 1956) assumes that one set of parameters is free of error to permit unique determination of the projection onto the line of best fit. Regressions were made both ways using first the chemical compositions and then the cell dimensions as fixed parameters. Fortunately, the general conclusions are essentially independent of the choice of regression.

In choosing the chemical parameters it was assumed that the composition can be represented as  $(\text{Mg, Fe}^{2+}, \text{Mn, Ca})_2\text{SiO}_4$ . Thus Si was assumed to be unsubstituted and the olivine structure to be free of hole or interstitial defects. Mg, Mn, and Ca were chosen as the variable parameters and Fe and Si assumed to be fully determined from knowledge of the three variables. Nickel was neglected and was thus assumed to have the same effect as iron.

Ideally the coefficients relating the three chemical parameters to the three dimensional parameters should be sufficiently larger than the errors for it to be possible to provide a method for estimating accurately the chemical composition of an olivine from its cell dimensions, and to provide data for testing crystal-chemical arguments on the substitution

of one cation by another. Unfortunately the coefficients for Mn and Ca are uncertain because of the small ranges of substitution; moreover, Mn is strongly correlated with Fe as might be expected from crystal-chemical arguments. Consequently a second approach was made in which the cell dimensions were 'adjusted' to those for an ideal (Mg,Fe) olivine series, free of Mn and Ca. It was assumed that the substitution of small amounts of Ca and Mn in (Mg,Fe) olivine leads to linear changes in the cell dimensions towards those of  $\text{Mn}_2\text{SiO}_4$  (tephroite),  $\text{CaMgSiO}_4$  (monticellite), and natural kirschsteinite. This assumption will not be valid if non-linear changes occur, such as those found in the tephroite-lithiophilite series (Bradley, Engel, and Munro, 1966). Such non-linear changes would be expected in ordered cation arrays. Unfortunately monticellite has ordered Ca and Mg atoms, thus making unlikely the assumption of linearity: perhaps the cell volume changes linearly even if the individual cell dimensions do not.

Upon receiving the original manuscript describing regressions carried out by conventional procedures, Dr. M. H. Hey, Editor of the 'Mineralogical Magazine', kindly pointed out that he was developing a new procedure for obtaining best fits for multivariate correlations. The details of the procedure, which involves complex calculations, will be given elsewhere. Briefly the errors of all the variables are treated simultaneously. Estimates are made of the standard errors of each variable on the basis of the experimental details and the variables are normalized by dividing them by the estimated errors. If there are  $m$  chemical variables, and a total of  $n$  physical and chemical variables, the best-fitting  $(n-m)$ -flat in  $n$ -dimensional space is calculated. Mathematically this is accomplished by solving a matrix of the sums of squares and products of all the variables (using standardized and weighted differences from the mean). The  $m$ -latent vectors corresponding to the smallest latent roots define the best  $(n-m)$ -flat. Since the chemical terms sum to unity when mole fractions are used (this assumes either that there are no defects or that the total number of defects is constant), the matrix is singular, and one root will be zero. From the set of equations, any chosen variables can be eliminated to yield equations relating any of the  $n$  variables to any  $(m-1)$  others. These derived equations are mutually consistent and statistically unbiased. The final results do not differ greatly from the mean of standard regression equations obtained by first assuming that the chemical data are free of error and then assuming that the physical data are free of error.

In this paper only the data obtained by Hey's multivariate best-fit

programme will be given. Regression data can be readily obtained by a reader using a standard computer programme and the data in table I.

*Discussion of multivariate best-fit results*

The unadjusted cell dimensions and atomic fractions of table I were analysed assuming probable errors  $\epsilon_{\text{Fe}}$  and  $\epsilon_{\text{Mg}} 0.02$ ,  $\epsilon_{\text{Mn}}$  and  $\epsilon_{\text{Ca}} 0.001$ ,  $\epsilon_a 0.0013$ ,  $\epsilon_b 0.0014$ ,  $\epsilon_c 0.0006$ . There are 26 observations, which were assigned equal weight for simplicity. Examination of the residuals showed that the data for synthetic fayalite did not belong to the same population as those for the natural olivines, while those for synthetic forsterite did. Consequently a new analysis was made omitting the data for fayalite.

The correlation matrix:

Fe	1.0	-0.9997	0.7357	0.3221	0.9975	0.9985	0.9984
Mg		1.0	-0.7513	-0.3200	-0.9980	-0.9990	-0.9986
Mn			1.0	0.0213	0.7505	0.7512	0.7466
Ca				1.0	0.3401	0.3388	0.3241
<i>a</i>					1.0	0.9973	0.9973
<i>b</i>						1.0	0.9987
<i>c</i>							1.0

reveals that the pairs of terms  $r_{\text{Fe},a}$  and  $r_{\text{Mg},a}$ ,  $r_{\text{Fe},b}$  and  $r_{\text{Mg},b}$ ,  $r_{\text{Fe},c}$  and  $r_{\text{Mg},c}$ , are almost equal and opposite in sign. This is because Mn and Ca are too small in range to be truly effective. Manganese and Ca are not correlated, while Mn is quite strongly correlated positively with Fe. Calcium is also positively correlated with Fe, though only weakly (not significant at the 10 % level).

Writing  $(\text{Mg}-\bar{\text{Mg}})/\epsilon_{\text{Mg}} = \xi_{\text{Mg}}$  *et sim.*, where the means are found to be  $\bar{\text{Fe}} 0.38444$ ,  $\bar{\text{Mg}} 0.60460$ ,  $\bar{\text{Mn}} 0.00880$ ,  $\bar{\text{Ca}} 0.00216$ ,  $\bar{a} 4.78028$ ,  $\bar{b} 10.30846$ ,  $\bar{c} 6.02997$ , the best-fitting 3-flat in 7-dimensional space is defined by the four mutually orthogonal equations (cited with normalized coefficients,  $\sum \alpha^2 = 1$ ):

$$\begin{aligned}
 0 &= -0.2333\xi_{\text{Fe}} + 0.1883\xi_{\text{Mg}} + 0.0903\xi_{\text{Mn}} + \\
 &\quad + 0.8090\xi_{\text{Ca}} + 0.1204\xi_a - 0.3156\xi_b + 0.3651\xi_c, \\
 0 &= 0.3692\xi_{\text{Fe}} - 0.3723\xi_{\text{Mg}} + 0.0107\xi_{\text{Mn}} + \\
 &\quad + 0.0518\xi_{\text{Ca}} + 0.8064\xi_a - 0.2235\xi_b - 0.1487\xi_c, \\
 0 &= 0.5308\xi_{\text{Fe}} - 0.5473\xi_{\text{Mg}} + 0.0519\xi_{\text{Mn}} + \\
 &\quad + 0.2780\xi_{\text{Ca}} - 0.5560\xi_a - 0.1700\xi_b + 0.0290\xi_c, \\
 0 &= 0.7062\xi_{\text{Fe}} + 0.7062\xi_{\text{Mg}} + 0.3531\xi_{\text{Mn}} + 0.3531\xi_{\text{Ca}}.
 \end{aligned}$$

The sums of squared normal residuals are 76.6, 35.5, 9.7, and 0, respectively (note that the last equation is merely the standardized form of  $\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca} = 1$  with origin at the means—hence the residuals must be 0). The sum of squared normal residuals to the 3-flat is there-

TABLE I. Cell dimensions of olivine (in Å); estimated standard errors in parentheses.

Specimen	Chemical composition				a	b	c	V
	Mg	Mn		Ca				
		Atomic %						
Syn. Fo	1.000	0.000	0.000	0.000	4.7545(13)	10.2000(14)	5.9814(3)	290.08(6)
YS 31	0.952	0.002	0.000	0.000	4.7570(10)	10.2067(12)	5.9870(3)	290.68(5)
R 1839	0.913	0.001	0.000	0.000	4.7605(9)	10.2116(10)	5.9894(2)	291.16(4)
YS 29	0.904	0.001	0.000	0.000	4.7613(17)	10.2190(19)	5.9921(5)	291.55(7)
YS 28	0.901	0.001	0.001	0.001	4.7599(15)	10.2299(23)	5.9933(5)	291.85(7)
YS 27	0.891	0.001	0.000	0.000	4.7628(10)	10.2227(12)	5.9933(3)	291.81(5)
YS 25	0.885	0.001	0.001	0.001	4.7619(17)	10.2248(22)	5.9943(6)	291.85(8)
YS 24	0.878	0.003	0.000	0.000	4.7631(10)	10.2351(16)	5.9975(4)	292.38(5)
YS 23	0.878	0.002	0.005	0.005	4.7636(15)	10.2376(19)	5.9989(6)	292.55(7)
YS 21	0.871	0.003	0.001	0.001	4.7646(10)	10.2360(12)	5.9983(3)	292.54(5)
YS 19	0.803	0.003	0.005	0.005	4.7698(12)	10.2558(10)	6.0070(8)	293.85(5)
YS 18	0.758	0.003	0.004	0.004	4.7740(15)	10.2660(18)	6.0133(12)	294.71(7)
R 2287	0.755	0.003	0.001	0.001	4.7723(17)	10.2643(21)	6.0147(16)	294.62(8)
YS 14	0.609	0.007	0.006	0.006	4.7787(10)	10.3168(15)	6.0315(4)	297.36(6)
YS 13	0.599	0.007	0.005	0.005	4.7839(18)	10.3133(25)	6.0295(14)	297.49(11)
YS 15	0.535	0.006	0.002	0.002	4.7832(13)	10.3227(14)	6.0337(10)	297.92(8)
YS 12	0.523	0.007	0.006	0.006	4.7849(13)	10.3275(10)	6.0391(12)	298.43(9)
YS 11	0.515	0.007	0.000	0.000	4.7860(14)	10.3304(18)	6.0400(12)	298.62(9)
YS 7	0.412	0.021	0.000	0.000	4.7912(16)	10.3642(14)	6.0550(11)	300.67(9)
YS 9	0.272	0.010	0.001	0.001	4.8002(15)	10.4028(19)	6.0748(6)	303.36(9)
YS 5	0.133	0.013	0.002	0.002	4.8099(15)	10.4420(8)	6.0892(4)	305.83(8)
R 2202	0.091	0.015	0.005	0.005	4.8122(19)	10.4524(16)	6.0945(4)	305.55(6)
YS 3	0.037	0.059	0.001	0.001	4.8161(26)	10.4689(43)	6.0974(13)	307.43(16)
YS 2	0.000	0.014	0.006	0.006	4.8176(4)	10.4820(5)	6.0995(7)	308.01(4)
YS 1	0.000	0.030	0.002	0.002	4.8177(7)	10.4789(12)	6.1046(4)	308.19(6)
Syn. Fa.	0.000	0.000	0.000	0.000	4.8186(8)	10.4822(23)	6.1108(20)	308.65(9)

fore 121.8, and with 25 observations of equal weight the root-mean-square standardized residual is 2.9. Since this value should be 1 for variables linearly related with errors correctly estimated, *either* the variables are not quite linearly related *or* the errors have been underestimated, *or* both. Since evidence is given later for no significant non-linearity, under-estimation of errors seems to be the main cause.

The above orthogonal equations yield by linear combination 35 equations that are exactly consistent with the best-fitting 3-flat, and with each other. Ten equations are of principal interest, as follows (the under-listed standard errors are nearly correct, but may require some small adjustments):

$$a = 4.7556 + 0.0621 \text{ Fe} + 0.11 \text{ Ca} + 0.067 \text{ Mn} \pm 0.0014 \quad (1)$$

$$= 4.8177 - 0.0621 \text{ Mg} + 0.05 \text{ Ca} + 0.005 \text{ Mn} \pm 0.0014 \quad (2)$$

$$b = 10.1946 + 0.2759 \text{ Fe} + 1.87 \text{ Ca} + 0.423 \text{ Mn} \pm 0.0043 \quad (3)$$

$$= 10.4705 - 0.2759 \text{ Mg} + 1.59 \text{ Ca} + 0.147 \text{ Mn} \pm 0.0043 \quad (4)$$

$$c = 5.9823 + 0.1274 \text{ Fe} - 0.64 \text{ Ca} + 0.013 \text{ Mn} \pm 0.0030 \quad (5)$$

$$= 6.1096 - 0.1274 \text{ Mg} - 0.77 \text{ Ca} - 0.114 \text{ Mn} \pm 0.0030 \quad (6)$$

$$\text{Mg} = 83.09 - 18.304a + 0.532b - 0.078c \pm 0.03 \quad (7)$$

$$\text{Fe} = 130.28 - 78.694a + 11.790b + 20.687c \pm 0.13 \quad (8)$$

$$\text{Mn} = -242.59 + 110.36a - 14.369b - 22.690c \pm 0.17 \quad (9)$$

$$\text{Ca} = 30.21 - 13.359a + 2.047b + 2.080c \pm 0.02 \quad (10)$$

Plots of the residuals for all ten equations showed a featureless scatter about zero with no sign of curvature in any variable: hence higher-order terms are not required.

In equation (1), the coefficients for Fe and Mn are equal within the large error for Mn indicating that Mn could be combined with Fe: this is borne out by equation (2) in which the coefficient for Mn is insignificant as a result of the elimination of its near-equivalent Fe. The coefficients for Ca in both (1) and (2) are smaller than the error. Equations (3) and (4) show that Ca appears to affect *b* much more than it does *a*, while the coefficients of Mn appear distinct from those of Fe. The same applies to equations (5) and (6) for *c*.

If the three cell dimensions were not significantly correlated, they would suffice to determine the three independent compositional variables;

but since they prove to be highly correlated for the specimens studied, they cannot give a reliable guide to more than one chemical variable. It will be noted that while most of the coefficients in equations (7) to (10) are significantly different from zero, they all have large standard errors, as have the equations themselves, except for equation (7), for Mg.

The estimates of the cell dimensions of monticellite, tephroite, and kirschsteinite derived by extrapolation of equations (1) to (6) are compared with measured values in table II. Considering the small range of

TABLE II. Cell dimensions of some olivines, in Å, with estimated standard errors in parentheses, from the literature, compared with values extrapolated from equations (1) to (6)

	<i>a</i>	<i>b</i>	<i>c</i>	V	Ref.
Forsterite	4.7545(13)	10.2000(14)	5.9814(3)	290.08(6)	1
	4.756(5)	10.195(5)	5.981(10)	290.0	2
	4.7556	10.1946	5.9827	—	9
Fayalite	4.8186(8)	10.4822(2)	6.1108(2)	308.65(9)	1
	4.817(5)	10.477(5)	6.105(10)	308.1	2
	4.820(2)	10.485(5)	6.093(2)	307.9	3
	4.822	10.517	6.056	306.5	4
	4.82	10.47	6.08	307.2	5
	4.8177	10.4705	6.1096	—	9
Tephroite	4.8968(2)	10.590(5)	6.250(3)	324.1(3)	6
	4.901(2)	10.598(5)	6.257(2)	325.0	3
	4.822	10.617	5.996	—	9
Monticellite	4.822(1)	11.108(3)	6.382(2)	341.8	7
	4.811	11.129	5.663	—	9
Kirschsteinite	4.859(5)	11.132(5)	6.420(5)	347.3	8
	4.910	11.126	6.457	352.7	4
	4.842	11.263	5.727	—	9

1. This paper (observed).
2. Yoder and Sahama, 1957.
3. Santoro, Newnham, and Nomura, 1966.
4. Wyderko and Mazanek, 1968; syntheses from the melt.
5. Fisher, 1967; data estimated from graph.
6. Bradley, Engel, and Munro, 1966.
7. Onken, 1965.
8. Sahama and Hytonen, 1957; Ca:Fe:Mg:Mn = 0.96:0.77:0.23:0.04.
9. Extrapolated from equations (1) to (6).

Ca and Mn the agreement of calculated and measured values of *a* and *b* is unexpectedly good. However the very low calculated values of *c* resulting from the negative coefficients of Ca and Mn in equation (6) are remarkable, and would suggest that replacement of (Mg,Fe) by Ca and Mn reduces *c*, and that an increase only begins after replacement is appreciable, but the data unfortunately are too inadequate to be

definite. Measurement of further specimens, especially synthetic material, is desirable.

Since the data are inadequate to define all the chemical variations, the effects of Ca and Mn were arbitrarily adjusted by linear extrapolation to a pure (Mg,Fe) olivine from the observed cell dimensions of tephroite, monticellite, and kirschsteinite. This adjustment is probably reasonable for  $a$  and  $b$ , but may not be reasonable for  $c$  judging from the previous paragraph:  $a_{\text{adj.}} = a_{\text{obs.}} - 0.078 \text{ Mn} - 0.083 \text{ Ca}$ ;  $b_{\text{adj.}} = b_{\text{obs.}} - 0.108 \text{ Mn} - 1.45 \text{ Ca}$ ;  $c_{\text{adj.}} = c_{\text{obs.}} - 0.139 \text{ Mn} - 0.66 \text{ Ca}$ . The new means are  $\bar{Mg}$  0.6046,  $\bar{Fe}$  0.3954,  $\bar{a}$  4.77942,  $\bar{b}$  10.30437,  $\bar{c}$  6.02732, and the estimated errors are unchanged, except for  $\epsilon_c$ , which was increased to 0.0008.

The curve of best fit is now a straight line (a 1-flat) in 5-space defined by four orthogonal normalized equations:

$$\begin{aligned} 0 &= 0.1053\xi_{\text{Fe}} - 0.1053\xi_{\text{Mg}} - 0.0492\xi_a + 0.5595\xi_b - 0.8139\xi_c, \\ 0 &= 0.3399\xi_{\text{Fe}} - 0.3399\xi_{\text{Mg}} + 0.8257\xi_a - 0.2599\xi_b - 0.1406\xi_c, \\ 0 &= 0.5801\xi_{\text{Fe}} - 0.5801\xi_{\text{Mg}} - 0.5334\xi_a - 0.2012\xi_b + 0.4408\xi_c, \\ 0 &= 0.7071\xi_{\text{Fe}} + 0.7071\xi_{\text{Mg}}. \end{aligned}$$

The sums of standardized squared normal residuals 139.2, 45.2, 11.4, and 0, respectively, give a total sum of squared normal residuals to the line of 195.3, and a r.m.s. standardized residual of 3.1. As before this suggests either curvature or under-estimated error: again no evidence of curvature arises from plots of the residuals.

Since all linear combinations of the above equations are mutually consistent it is sufficient to quote merely three equations relating the cell dimensions to Mg.

$$a = 4.8157 - 0.05995 \text{ Mg} \pm 0.0015, \quad (11)$$

$$b = 10.4721 - 0.2774 \text{ Mg} \pm 0.0042, \quad (12)$$

$$c = 6.09811 - 0.1171 \text{ Mg} \pm 0.0028. \quad (13)$$

These may be combined to yield the cell volume  $V$ :

$$V = 307.5 - 17.88 \text{ Mg}. \quad (14)$$

If  $a$ ,  $b$ ,  $c$  have all been measured, the best estimate of Mg will be obtained by taking the three separate estimates of Mg from equations (11)–(13) and weighting them according to the assessed accuracy of the cell dimensions:

$$\text{Mg} = \frac{(80.333 - 16.682a)/\epsilon_a^2 + (37.755 - 3.6053b)/\epsilon_b^2 + (52.085 - 8.5412c)/\epsilon_c^2}{1/\epsilon_a^2 + 1/\epsilon_b^2 + 1/\epsilon_c^2}.$$

### *Conclusion*

The present evidence for linearity of the cell dimensions in relation to the principal chemical substitution, Mg for Fe, confirms the implications from other techniques that natural olivines have disordered Mg and Fe, and that the olivine series contains an ideal or near-ideal solid solution. It should be emphasized that the chemical compositions used in the regressions are based on microprobe analyses by Smith (1966). Since these analyses were referred to synthetic olivines, the real control on the chemical composition is the accuracy of preparation of the synthetic olivines.

The 'relatively sharp break' from a linear relation between spacing and composition found by Jambor and C. H. Smith (1964) probably arises from the effects of substituting Ca and Mn, and perhaps from some errors in the chemical composition. Fisher (1967) has reported a slight systematic curvature for  $a$ ,  $c$ , and  $V$  as a function of Mg content for six synthetic olivines, while the relation between  $b$  and Mg was essentially linear. Until full details appear, it is not possible to assess the experimental errors in his work.

As mentioned earlier the data for synthetic fayalite were withdrawn from the best-fit analysis because the cell dimensions were much too high to fit with the other data. Santoro, Newnham, and Nomura (1966) and Fisher (1967) obtained lower  $c$  values: indeed Fisher's value would fit well with the present data for natural olivines 'adjusted' for Ca and Mn substitution. The three sets of measurements for  $a$  and  $b$  are consistent within the experimental errors. From the variation in  $c$  it seems likely that the fayalite is affected by the method of synthesis: the present specimen came from a blast furnace whereas Fisher's was prepared hydrothermally in a buffered system at much lower temperatures. Chudoba and Frechen (1943) and Yoder and Sahama (1957) have previously discussed the possibility of two forms of fayalite. Smith and Stenstrom (1965) have suggested a coupled substitution replacing  $\text{Mg}^{2+}\text{Si}^{4+}$  by  $2\text{Fe}^{3+}$ . This substitution would be favoured by conditions in a blast furnace, but not in Fisher's buffered system.

The present data show that it is quite impractical to estimate all three principal substituents in olivines from measured cell dimensions. Even an estimate of Mg only (thereby assuming that Mn and Ca are equivalent to Fe) is subject to unknown errors, which may be serious if Mn and Ca are high. Since the substitution of Mn and Ca tends to be greater in Fe-rich olivines, and relatively small in Mg-rich olivines,

reasonably accurate estimates of the Mg-content can be obtained from the cell dimensions for the latter. Perhaps in routine work such estimates may be accurate to 0.01–0.02 in Mg. For Fe-rich olivines gross errors can arise from unfavourable specimens. For some rock types where unusual amounts of Ca and Mn are unlikely, reasonable estimates even of Fe-rich olivines may be obtained for the Mg content. The forthcoming survey of minor-element content in olivines by T. Simkin and J. V. Smith (see abstract in the 1966 programme of the Geological Society of America) provides a guide. For a petrographer working on a homogeneous suite of olivines, a simple technique like that of Jackson (1960) or Jambor and C. H. Smith (1964) may be quite valuable.

No evidence has been found here for extra lines in X-ray patterns of olivine, and it is concluded that the claims of Eliseev (1958) are spurious.

Olivine, unlike most rock-forming silicates, seems to be a simple substance with a simple structure, and its apparent complexities as recorded in the older literature are the result merely of human frailty.

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#### References

- AGTERBERG (F. P.), 1964. *Min. Mag.*, vol. 33, p. 742 [M.A. 16–565].
- BIRLE (J. D.), GIBBS (G. V.), MOORE (P. B.), and SMITH (J. V.), 1968. *Amer. Min. vol. 53*, p. 807.
- BLOSS (F. D.), 1952. *Amer. Min.*, vol. 37, p. 966 [M.A. 12–317].
- BRADLEY (R. S.), ENGEL (P.), and MUNRO (D. C.), 1966. *Min. Mag.*, vol. 35, p. 742 [M.A. 17–577].
- BURNHAM (C. W.), 1962. *Ann. Rept. Dir. Geophys. Lab., Year Book 61*, p. 132.
- CHUDOBA (K. F.) and FRECHEN (J.), 1943. *Neues Jahrb. Min., Monats., Abt. A*, p. 91 [M.A. 9–153].
- DUKE (D. A.) and STEPHENS (J. D.), 1964. *Amer. Min.*, vol. 49, p. 1388.
- [ELISÉEV (E. N.)] ЕЛИССЕВ (Э. Н.) 1958. *Кристаллография*, vol. 3, p. 167; transl. as *Soviet Physics (Crystallography)*, vol. 3, p. 163.
- FISHER (G. W.), 1967. *Ann. Rept. Dir. Geophys. Lab., Year Book 65*, p. 209.
- GHOSE (S.), 1962. *Amer. Min.*, vol. 47, p. 388.
- GIBBS (G. V.), MOORE (P. B.), and SMITH (J. V.), 1964. *Geol. Soc. Amer.*, spec. paper no. 76, p. 66.
- HENRIQUES (Å.), 1957. *Arkiv Min. Geol.*, vol. 2, p. 305.
- HEY (M. H.), 1956. *Min. Mag.*, vol. 31, p. 69.
- JACKSON (E. D.), 1960. *U.S. Geol. Surv. Prof. Paper 400B*, p. B432 [M.A. 15–219].
- JAMBOR (J. L.) and SMITH (C. H.), 1964. *Min. Mag.*, vol. 33, p. 730.
- LEHMANN (H.), DUTZ (H.), and KOLTERMANN (M.), 1961. *Ber. deutsch. keram. Gesell.*, vol. 38, p. 512.
- NAFZIGER (R. H.) and MUAN (A.), 1967. *Amer. Min.*, vol. 52, p. 1364 [M.A. 19–110].
- ONKEN (H.), 1965. *Tschermaks Min. Petr. Mitt.*, ser. 3, vol. 10, p. 33 [M.A. 17–560].
- SAHAMA (TH. G.) and HYTÖNEN (K.), 1957. *Min. Mag.*, vol. 31, p. 698.

- SAHAMA (TH. G.) and TORGESON (D. R.), 1949. Rept. Invest. U.S. Bur. Mines, no. 4408 [M.A. 11-145].
- SANTORO (R. P.), NEWNHAM (R. E.), and NOMURA (S.), 1966. Journ. Phys. Chem. Solids, vol. 27, p. 655.
- SMITH (J. V.), 1956. Min. Mag., vol. 31, p. 47.
- 1966. Journ. Geol., vol. 74, p. 1 [M.A. 18-190].
- and STENSTROM (R. C.), 1965. Min. Mag., vol. 34, p. 436.
- WYDERKO (M.) and MAZANEK (E.), 1968. *Ibid.*, vol. 36, p. 955.
- YODER (H. S., JR.) and SAHAMA (TH. G.), 1957. Amer. Min., vol. 42, p. 475 [M.A. 14-146].

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