

## CELL DIMENSIONS AND X-RAY DETERMINATIVE CURVE FOR SYNTHETIC Mg-Fe OLIVINES

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## ABSTRACT

Twelve olivines of the  $(\text{Mg}_x\text{Fe}_{1-x})_2\text{SiO}_4$  solid solution series, six synthesized hydrothermally at 500 bars, and six at 2000 bars, were used to determine the variation of olivine unit-cell dimensions with mole fraction  $\text{Mg}_2\text{SiO}_4$ , and to calibrate an X-ray determinative curve based on the variation of  $d(130)$  with composition. In both groups of olivines,  $b$  is a linear function of composition, but plots of  $a$ ,  $c$ ,  $V$ , density, and molar volume against mole fraction  $\text{Mg}_2\text{SiO}_4$  are slightly curved and convex upwards, showing a small positive  $\Delta\rho$  of mixing. The regression equation for cell volume ( $V$ ,  $\text{\AA}^3$ ) is:  $V = 307.23 - 15.49x - 2.02x^2$ , where  $x$  is mole fraction  $\text{Mg}_2\text{SiO}_4$ . The best determinative curve for estimating  $x$  from measured values of  $d(130)$  (in  $\text{\AA}$ ) is:  $x = 15.8113\sqrt{3.0358 - d(130)} - 7.2250$ , with 95 percent tolerance limits for estimation of  $x$  of about  $\pm 0.02$ . Plots of  $d(130)$  and density against composition for the synthetic olivines agree closely with published data on natural magnesian olivines; however, natural iron-rich olivines have notably larger unit-cell dimensions (lower densities) than the synthetic olivines, probably because of substitution of  $\text{Ca}^{2+}$  and  $\text{Mn}^{2+}$  for  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  in the octahedral positions.

## INTRODUCTION

While conducting hydrothermal experiments in the system Mg-Fe-Si-O-H, we both independently synthesized six members of the  $\text{Mg}_2\text{SiO}_4$  (forsterite)- $\text{Fe}_2\text{SiO}_4$  (fayalite) olivine solid solution series, determined their unit-cell parameters from powder diffraction data, and prepared determinative curves based on the variation in  $d(130)$  with composition. We based our determinative curves on X-ray properties, rather than on refractive indices, because most of our synthetic olivines are too fine-grained for reliable optical measurements.

A number of authors (Eliseev, 1957; Yoder and Sahama, 1957; Heckrodt, 1958; Hotz and Jackson, 1963; Jambor and Smith, 1964; and Nafziger and Muan, 1967) have attempted to relate the X-ray properties of olivine to its composition. However, most of these studies are not strictly applicable to the pure Mg-Fe synthetic olivines because they were based on natural olivines, which commonly contain minor amounts of Ca, Mn, Cr, Ni, Ti, and  $\text{Fe}^{3+}$ . The only X-ray studies on pure Mg-Fe olivines appear to be complete unit-cell determinations for pure forsterite and fayalite (Yoder and Sahama, 1957), and measurements of  $d(131)$  and  $d(112)$  for forsterite, fayalite and three intermediate olivines (Nafziger and Muan, 1967).

The responsibility for the various sections of this paper is as follows: Medaris synthesized the olivines grown at 500 bars pressure, and measured their X-ray patterns. Fisher synthesized the olivines grown at 2000 bars, measured their X-ray patterns, computed the unit cell parameters of all the olivines, and performed the statistical treatment of the data.

### OLIVINE SYNTHESIS AND X-RAY METHODS

The olivines were synthesized hydrothermally from stoichiometric mixtures under the conditions given below. X-ray examination of the run products showed only olivine peaks, but optical examination revealed traces of orthopyroxene, anthophyllite, and an opaque mineral, presumably magnetite. These phases reflect minor oxidation of the starting mixture, which would tend to enrich the final olivine in  $Mg_2SiO_4$ ; but because only traces of these phases are present, the olivines synthesized are estimated to be within  $\pm 1$  mole percent of the starting compositions. X-ray patterns for the olivines were indexed by comparison with XRDF cards (7-75, 7-216, 9-484), Swanson and Tatge (1953, p. 83-84), Swanson, Gilfrich and Cook (1956, p. 32-34), and Yoder and Sahama (1957, p. 476-477). For each sample, 6 to 11 X-ray peaks were measured as described below, including 020, 021, 101, 130, 131, 112, 211, and others wherever possible. Unit cell parameters  $a$ ,  $b$ ,  $c$  and  $V$ , were calculated from these data on an IBM 7094 computer, using a least squares program written by C. W. Burnham (1962).

*2000 bar experiments (G. W. F.)* Weighed mixes of metallic iron, magnesium oxide fired for one hour at 1500°C, and purified quartz were homogenized by grinding under alcohol in an agate mortar for one hour, sealed with  $H_2O$  in an Ag capsule, and held for two weeks at 700°C and 2000 bars fluid pressure in cold seal pressure vessels. The olivines produced were mixed with  $CaF_2$  ( $a = 5.4626 \text{ \AA}$ ) as an internal standard, mounted on glass slides with Duco cement dissolved in acetone, and X rayed on a Norelco X-ray diffractometer using unfiltered Fe radiation. Each sample was scanned once at a scan speed of  $1/4^\circ 2\theta$  per minute, and a chart speed of 1/2 in/min; midpoints of  $FeK\alpha$  peaks at about  $2/3$  peak height were measured to the nearest  $0.002^\circ 2\theta$ . Values for  $2\theta(130)$  were measured separately by oscillating five times (ten measurements) between 130 of olivine and 111 of  $CaF_2$  (scan speed  $1/2^\circ 2\theta$  per minute, chart speed 1/2 in/min,  $2\theta$  measured to  $0.005^\circ 2\theta$  and averaged). It is assumed that small differences between  $2\theta$  values measured while scanning "up" (increasing  $2\theta$  values) and values measured scanning "down" are compensated by averaging equal numbers of "up" and "down" scans.

*500 bar experiments (L.G.M.)* Weighed mixes of metallic iron, magnesium oxide and cristobalite were sealed with  $H_2O$  inside an  $Ag_{70}Pd_{30}$  capsule, which was in turn sealed with  $H_2O$ , fayalite, magnetite, and quartz inside an Au capsule to maintain a fixed  $f_{O_2}$  (cf. Eugster and Wones, 1962). Runs were held at 900°C and 500 bars fluid pressure for approximately three weeks; all were removed at one week intervals, ground in an agate mortar to facilitate reaction and placed in a new capsule with a fresh buffer assemblage. The olivines produced were mixed with Si ( $a = 5.4301 \text{ \AA}$ ) as an internal standard, sedimented on glass slides with acetone, and X rayed with Mn-filtered  $FeK$  radiation on a Norelco diffractometer equipped with scintillation counter and pulse height analyzer. For each sample, four oscillations (eight measurements) were made (scan speed of  $1/4^\circ 2\theta$  per minute, chart speed 1/2 in/min); peaks were measured to the nearest  $0.002^\circ 2\theta$ , and the results averaged. For most peaks, the extreme values differ by less than  $0.01^\circ 2\theta$ .

## UNIT-CELL PARAMETERS

The olivines synthesized at 500 bars pressure have essentially the same unit-cell parameters as the olivines of the same composition synthesized at 2000 bars (Table 1). The cell dimensions of pure forsterite and fayalite agree within experimental error with those reported by Yoder and Sahama (1957, p. 477), and the dimensions of the intermediate olivines vary smoothly with composition (Figs. 1 and 2). In both groups,  $b$  is a linear function of mole fraction  $Mg_2SiO_4$ , but the plots of  $a$ ,  $c$  and  $V$  are slightly curved; in each case the cell parameters of the intermediate

TABLE 1. UNIT CELL PARAMETERS, DENSITY, MOLAR VOLUME AND  $d(130)$  FOR SYNTHETIC OLIVINES<sup>a</sup>

		Mole Fraction $Mg_2SiO_4$					
		0.0	0.2	0.4	0.6	0.8	1.0
500	Bars						
$a$	Å	4.815 (4)	4.810 (1)	4.798 (1)	4.784 (1)	4.769 (1)	4.753 (1)
$b$	Å	10.490 (9)	10.419 (1)	10.367 (3)	10.308 (1)	10.261 (3)	10.196 (1)
$c$	Å	6.085 (8)	6.068 (1)	6.047 (2)	6.024 (1)	6.006 (2)	5.979 (1)
$V$	Å <sup>3</sup>	307.3 (4)	304.08 (6)	300.8 (1)	297.09 (4)	293.9 (1)	289.76 (4)
$D_x$	g/cm <sup>3</sup> ± 0.017	4.404	4.175	3.942	3.710	3.465	3.225
$v$	cm <sup>3</sup>	46.28 (6)	45.79 (1)	45.30 (2)	44.73 (1)	44.26 (2)	43.63 (1)
$d(130)$	Å	2.8268	2.8153	2.8037	2.7907	2.7790	2.7645
2000	Bars						
$a$	Å	4.819 (5)	4.813 (1)	4.797 (4)	4.785 (1)	4.768 (1)	4.751 (2)
$b$	Å	10.470 (5)	10.417 (2)	10.358 (4)	10.309 (1)	10.252 (2)	10.197 (3)
$c$	Å	6.086 (3)	6.067 (1)	6.048 (2)	6.027 (1)	6.000 (1)	5.979 (1)
$V$	Å <sup>3</sup>	307.1 (1)	304.18 (5)	300.5 (1)	297.30 (4)	293.29 (6)	289.6 (1)
$D_x$	g/cm <sup>3</sup> ± 0.017	4.407	4.174	3.947	3.707	3.472	3.227
$v$	cm <sup>3</sup>	46.24 (2)	45.80 (1)	45.24 (2)	44.77 (1)	44.16 (1)	43.61 (2)
$d(130)$	Å	2.8271	2.8155	2.8021	2.7911	2.7777	2.7656

<sup>a</sup>  $V$  is unit cell volume,  $v$  is molar volume, and  $D_x$  is density calculated from  $V$ . Errors indicated in parentheses for unit cell parameters are the standard deviation given by the least squares program used to calculate the cell parameters (Burnham, 1962); error calculated for densities assumes 1% uncertainty in composition.

olivines are slightly larger than the proportionate sum of the end member parameters.

The curvature in the plots of  $a$ ,  $c$  and  $V$  is slight, but it appears to be real, because (1) it appears in both sets of olivines, synthesized and measured independently, and (2) most of the X-ray peaks on which the unit cell parameters are based are  $hk0$ ,  $0kl$ , or  $hkl$  peaks, so that any systematic calibration errors should be reflected in  $b$  as well as in  $a$  and  $c$ .

The statistical significance of the curvature can be evaluated by calculating quadratic regression equations for the unit-cell parameters

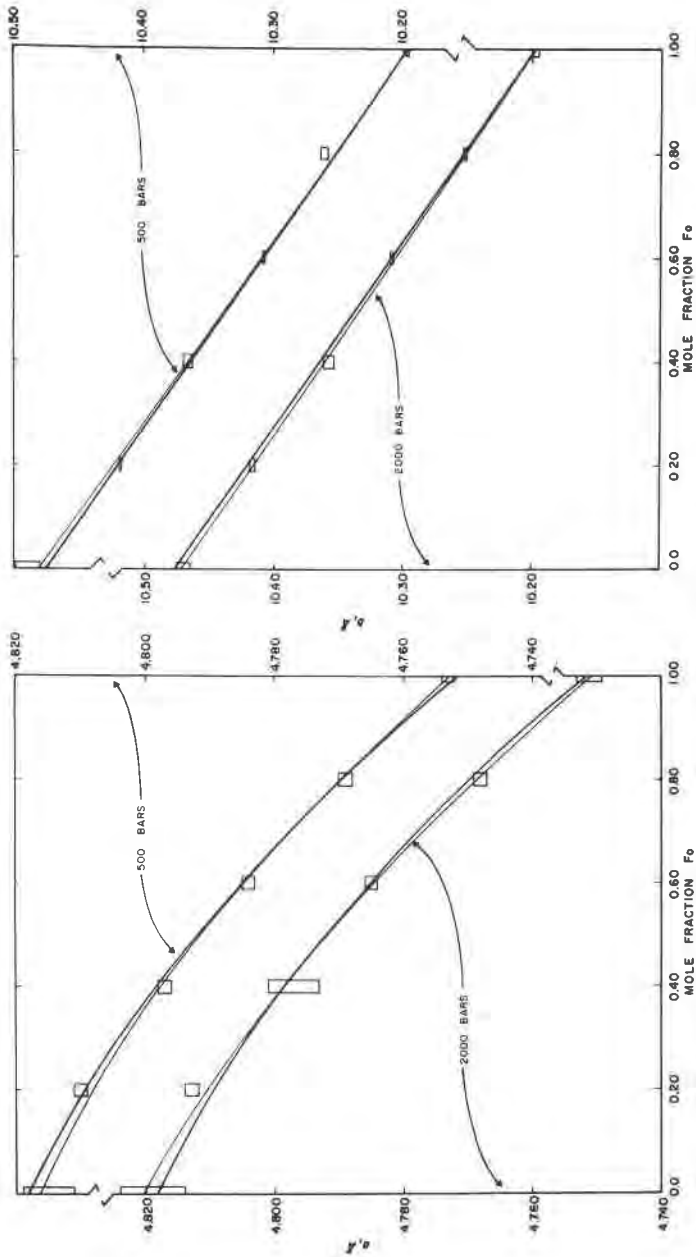


FIG. 1. Plot of unit-cell parameters  $a$  and  $b$  against composition for synthetic olivines. Note that scale on ordinate differs for each plot, and that the two groups of data are referred to different origins. Light lines represent regression equations calculated for each group of 6 olivines separately; heavy lines represent regressions calculated using all 12 measurements. Size of symbols represents calculated standard deviation.

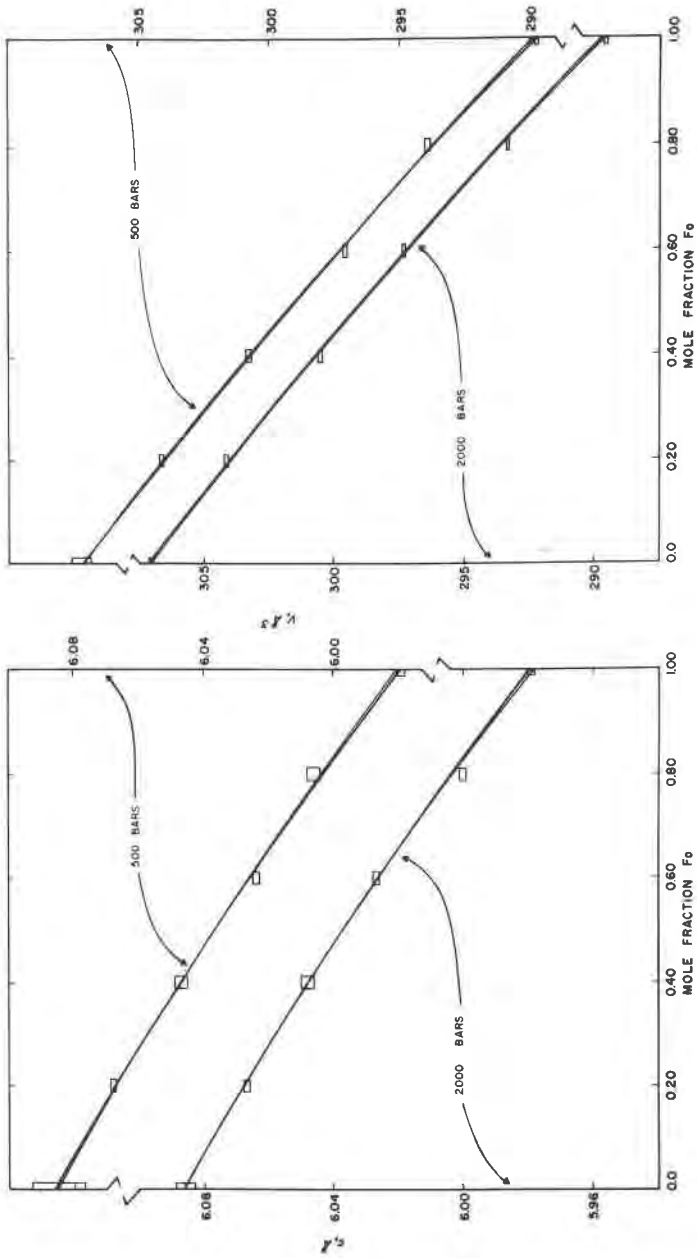


FIG. 2. Plot of unit-cell parameters  $\epsilon$  and  $V$  against composition. See legend for Fig. 1.

against composition, and then evaluating the significance of the coefficients of the  $x^2$  terms by forming the  $F$ -ratio between the mean sum of squares due to deviations about the regression and the mean sum of squares due to the quadratic term (Ostle, 1954, p. 141). In regression equations for  $a$ ,  $c$  and  $V$  in the two groups of olivines treated separately, the coefficient of the  $x^2$  term is significant at levels ranging from 0.90 to 0.98 (Table 2). Put differently, the probability of obtaining such a large deviation from linearity by chance is 0.10 to 0.02. The coefficient of the  $x^2$  term in regressions for  $b$  is not significant as would be expected from Figure 1, and the regression equations for  $b$  have been recalculated in linear form (Table 2).

The significance of the  $x^2$  coefficients is even larger (0.99 to 0.999) if regression equations are calculated for the combined data from both groups of olivines (Table 2). It seems reasonable to combine the data in this fashion, despite the fact that the two groups of olivines were synthesized under different conditions, because (1) the unit-cell parameters of both groups were measured under the same conditions, namely room temperature and one atmosphere pressure, and (2) the unit-cell data and the regression equations for the two groups of olivines, treated individually, are nearly identical; the coefficients in the regression equations for the 500 bar olivines differ by less than their standard errors from those in the corresponding equations for the 2000 bar olivines, and the constant terms are within experimental uncertainty. The only suspiciously large differences between these equations are due almost entirely to the relatively large difference in  $b$  of the two pure fayalites. Of all the olivines measured, these two gave the poorest diffraction patterns, with relatively broad, poorly defined peaks, and have the largest errors in their unit-cell parameters (Table 1, Fig. 1); probably the differences between them are not significant.<sup>1</sup>

#### OLIVINE DETERMINATIVE CURVE

In principle, the variation in unit-cell dimensions with composition could be used to estimate olivine compositions. However, this approach would require measuring a large number of olivine peaks, which is difficult to do in mixtures of olivine with other phases. Therefore, we chose the variation of  $d(130)$  with olivine composition as the basis for a deter-

<sup>1</sup> The difference between the two groups of data can also be evaluated statistically, using a procedure brought to our attention by Dr. Leon Gleser, of the Statistics Department, Johns Hopkins University. By comparing the mean sum of squares due to deviation about the regression equations for the separate groups of olivines with the mean sum of squares due to deviations about the regression for the combined data, it can be shown that there are no significant differences between the two sets of measurements.

TABLE 2. REGRESSION EQUATIONS OF OLIVINE X-RAY PARAMETERS AGAINST COMPOSITION

	Regression equation <sup>a</sup> with standard errors of coefficients	Significance of $x^2$ coefficient
$a_{500}$	$= 4.8161 - 0.0299x - 0.0299x^2$ $\pm 0.0065 \pm 0.0062$	0.98
$a_{2000}$	$= 4.8201 - 0.0432x - 0.0263x^2$ $\pm 0.0083 \pm 0.0079$	0.95
$a_{\text{comb}}$	$= 4.8181 - 0.0386x - 0.0281x^2$ $\pm 0.0056 \pm 0.0054$	0.999
$b_{500}$	$= 10.4832 - 0.2861x$ $\pm 0.0075$	0.40
$b_{2000}$	$= 10.4702 - 0.2727x$ $\pm 0.0025$	0.10
$b_{\text{comb}}$	$= 10.4767 - 0.2794x$ $\pm 0.0050$	0.20
$c_{500}$	$= 6.0854 - 0.0886x - 0.0170x^2$ $\pm 0.0085 \pm 0.0082$	0.90
$c_{2000}$	$= 6.0861 - 0.0894x - 0.0188x^2$ $\pm 0.0078 \pm 0.0075$	0.92
$c_{\text{comb}}$	$= 6.0857 - 0.0890x - 0.0179x^2$ $\pm 0.0050 \pm 0.0048$	0.99
$V_{500}$	$= 307.30 - 15.57x - 1.88x^2$ $\pm 0.84 \pm 0.81$	0.90
$V_{2000}$	$= 307.16 - 15.41x - 2.17x^2$ $\pm 0.88 \pm 0.85$	0.92
$V_{\text{comb}}$	$= 307.23 - 15.49x - 2.02x^2$ $\pm 0.59 \pm 0.56$	0.99
$[d(130)]_{500}$	$= 2.8267 - 0.0550x - 0.0069x^2$ $\pm 0.0023 \pm 0.0022$	0.94
$[d(130)]_{2000}$	$= 2.8274 - 0.0617x$ $\pm 0.0007$	0.20
$[d(130)]_{\text{comb}}$	$= 2.8270 - 0.0578x - 0.0040x^2$ $\pm 0.0018 \pm 0.0017$	0.96

<sup>a</sup>  $x$  = mole fraction  $\text{Mg}_2\text{SiO}_4$  in olivine,  $a$ ,  $b$ ,  $c$ ,  $d(130)$  given in  $\text{\AA}$ ,  $V$  given in  $\text{\AA}^3$ . The equations for parameters of olivines grown at 500 bars and at 2000 bars are each based on 6 samples (3 degrees of freedom due to deviation about quadratic regression); those for both groups of olivines combined are based on 12 samples (9 degrees of freedom due to deviation about quadratic regression.)

minative curve, because (1) the 130 peak is sufficiently intense to appear in mixtures containing as little as ten percent olivine; (2) the 130 peak is not overlapped by peaks of the other principal phases in the system Mg-Fe-Si-O-H; (3)  $d(130)$  varies enough to permit reasonably precise estimates of composition. For similar reasons, Yoder and Sahama (1957) chose the 130 peak for estimating the compositions of natural olivines.

Values of  $d(130)$  (Table 1) vary smoothly with olivine composition (Fig. 3, Table 2). The calculated significance level for the  $x^2$  coefficient in the regression equation for  $d(130)$  of the olivines grown at 500 bars (0.94) and for  $d(130)$  of the combined olivine data (0.96) suggest that the relation between  $d(130)$  and composition is slightly curved, although the olivines grown at 2000 bars do not reflect this curvature. The curvature is very slight, because for this peak the large linear variation of  $b$  nearly masks the small curved variation of  $a$ .

The regressions of Table 2 can be cast in a more useful form for estimating  $x$  from measurements of  $d(130)$  by solving for  $x$  in terms of  $d(130)$ . The solution for the regression based on the combined data from both groups of olivines is:

$$x = 15.8113\sqrt{3.0358 - d(130)} - 7.2250.$$

Using the combined data from both groups of olivines, 95 percent tolerance limits for estimation of  $d(130)$  from observations of olivine composition were calculated by multiplying  $t_{0.05}$  times the standard error for prediction of individual  $d(130)$  values (Ostle 1954, p. 217):

Mole Fraction Fo	0.0	0.2	0.4	0.6	0.8	1.0
95% Limits	$\pm 0.0016$	$\pm 0.0015$	$\pm 0.0015$	$\pm 0.0015$	$\pm 0.0015$	$\pm 0.0016$

These limits correspond to a precision of about  $\pm 0.02$  in estimating mole fraction Fo in olivines from measured values of  $d(130)$  (Fig. 3).

The variation in  $d(130)$  for natural olivine (Yoder and Sahama, 1957) is quite close to that for magnesium-rich synthetic olivines, but diverges markedly for compositions more iron-rich than Fo<sub>40</sub> (Fig. 3). Clearly, the determinative curve obtained in this study is valid only for synthetic olivines, and should not be used to estimate the composition of natural olivines.

Yoder and Sahama recognized a similar divergence between the determinative curve for natural olivine and a straight line drawn between the  $d(130)$  values for synthetic forsterite and fayalite. They found that  $d(130)$  for synthetic fayalite was 0.0035 Å smaller than the extrapolated  $d(130)$  for pure natural fayalite. Taking into account the minor element content of natural olivine, and considering that the synthetic fayalite was produced at temperatures over 1000°C, whereas the samples of natural iron-rich olivines probably crystallized at lower temperatures,



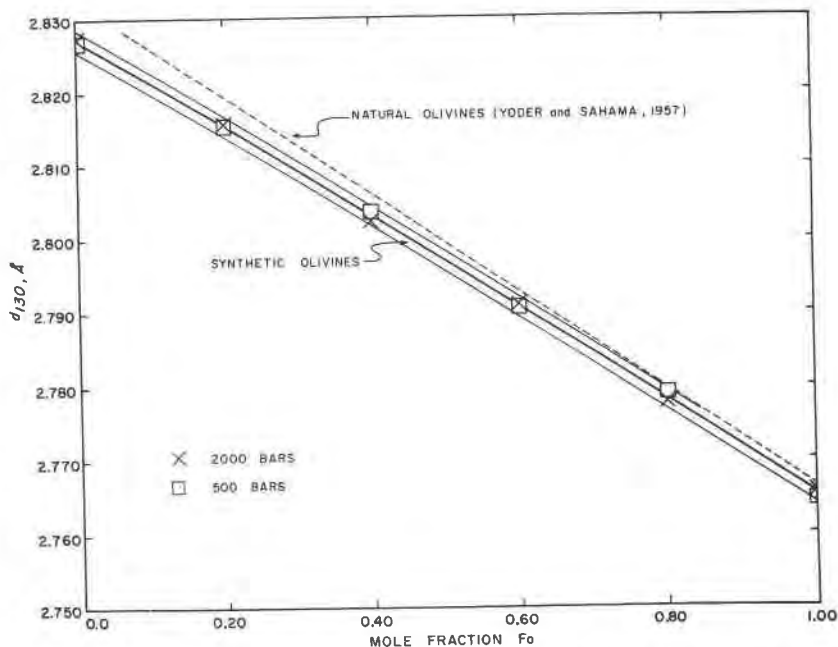


FIG. 3. Plot of  $d(130)$  against composition for synthetic olivines grown at 500 bars pressure (open boxes) and at 2000 bars pressure (crosses). Heavy solid line is least squares regression for synthetic olivines. Dashed line is regression curve for natural olivines, calculated by Yoder and Sahama (1957). Solid light lines show 95% tolerance limits for estimation of olivine composition, given a single value of  $d(130)$ . Size of symbol shows estimated error of each observation.

they suggested that the cell dimensions of iron-rich olivine might vary inversely with temperature. Values of  $d(130)$  for fayalite synthesized below  $1000^{\circ}\text{C}$  are about  $0.002 \text{ \AA}$  less than for fayalite produced over  $1000^{\circ}\text{C}$  (Table 3). This small difference may not be significant, since the determinations of  $d(130)$  were made in three separate laboratories; but in any

TABLE 3.  $d(130)$  OF SYNTHETIC FAYALITE

$T^{\circ}\text{C}$	$P$	Buffer	Preparation	$d(130)$
over $1000^{\circ}$	1 atm.	—	Blast furnace	2.8295 <sup>a</sup>
over $1000^{\circ}$	1 atm.	—	Dry fusion	2.8292 <sup>a</sup>
over $1000^{\circ}$	1 atm.	—	Dry fusion	2.8291 <sup>a</sup>
$900^{\circ}$	500 bars	FQI	Hydrothermal	2.8268
$900^{\circ}$	500 bars	FMQ	Hydrothermal	2.8265
$730^{\circ}$	2000 bars	—	Hydrothermal	2.8274

<sup>a</sup> Cited by Yoder and Sahama (1957).

case, the difference is in the wrong direction to explain the difference in  $d(130)$  between natural and synthetic olivine.

Jambor and C. H. Smith (1964, p. 737) and Agterberg (1964) re-examined Yoder and Sahama's data, and concluded that the variation in  $d(130)$  for natural olivines was nonlinear, with a break in slope near  $F_{0.30}$ . Jambor and Smith (1964, p. 740) suggested that this break might reflect "nonuniform variation in  $b$ ". This seems unlikely, however, in view of the linear variation in  $b$  of the synthetic olivines. Furthermore, the non-linearity reported by Jambor and Smith appears to be too large to be explained entirely by the curvature in  $a$  observed in the synthetic olivines. A likely explanation is that the break reflects nonuniform substitution of impurities in the natural olivines studied.

J. V. Smith and Stenstrom (1965, p. 452-455) and J. V. Smith (1966) have shown that the divergence between the determinative curves for natural and synthetic olivines can be accounted for by the presence in natural iron-rich olivines of minor amounts of  $Ca^{2+}$  and  $Mn^{2+}$ . They corrected the measured  $d(130)$  values of natural olivines to account for these impurities, and showed that the corrected values plot near a straight line between synthetic forsterite and fayalite. Their corrected values agree well with our data on synthetic olivines; of 32 corrected  $d(130)$  values for natural olivines, 30 plot within the 95 percent confidence limits for the synthetic olivine determinative curve (Fig. 3).

#### OLIVINE DENSITY

The density of synthetic olivine ( $D_x$ ) was calculated from the equation

$$D_x = \frac{MZ}{VN_A}$$

where  $D_x$  is in grams per cubic centimeter,  $M$  is the formula weight in grams,  $Z$  is the number of formula units per unit cell,  $V$  is the unit-cell volume in cubic centimeters, and  $N_A$  is Avogadro's number. The calculated densities vary smoothly with composition (Table 1, Fig. 4). The regression equation for density against composition, based on the combined data in Table 1, is

$$D_x = 4.4048 - 1.1353x - 0.0435x^2$$

where  $x$  is mole fraction forsterite; the significance of the  $x^2$  coefficient is 0.99.

A curve based on densities of thirty specimens of natural olivine (Bloss, 1952) is shown in Figure 4 for comparison with the density curve for

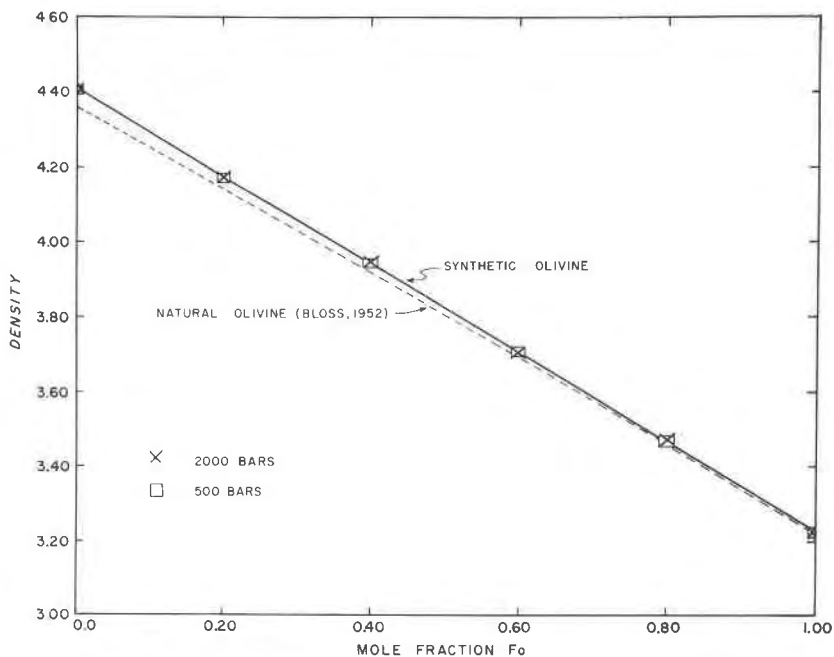


FIG. 4. Plot of density against composition for synthetic olivines grown at 500 bars pressure (open boxes) and at 2000 bars pressure (crosses). Heavy solid line is least squares regression for synthetic olivines. Dashed line is regression curve for natural olivines, after Bloss (1952). Size of symbol shows calculated error of observation, assuming 1% uncertainty in composition.

synthetic olivine. The two curves are quite close for magnesium-rich compositions but diverge for compositions rich in iron. This divergence reflects the fact that iron-rich synthetic olivine has smaller cell dimensions than does iron-rich natural olivine, as discussed earlier.

#### OLIVINE MOLAR VOLUME

The molar volumes ( $v$ ) of the synthetic olivines were calculated from the equation

$$v = \frac{VN_A}{Z}$$

where  $V$  is the unit cell volume in cubic centimeters,  $N_A$  is Avogadro's number, and  $Z$  is the number of formula units per unit cell. The calculated molar volumes vary smoothly with composition (Table 1) and show a slight convex upward curvature (positive  $\Delta v$  of mixing). The regression

for molar volume against composition, based on the combined data in Table 1, is

$$v = 46.263 - 2.338x - 0.302x^2$$

where  $x$  is the mole fraction forsterite; the significance of the  $x^2$  coefficient is 0.99.

In strictly ideal solutions the molar volume is a linear function of composition expressed in mole fractions (*e.g.*, Thompson, 1967, p. 345). Therefore, the apparent curvature of the relation between molar volume and composition for the synthetic olivines suggests that they are not an ideal solid solution series. Although early calorimetric data (Sahama and Torgeson, 1949) and density measurements (Bloss, 1952) suggested that the olivine solid solution was nearly ideal, recent experiments on the partitioning of Mg between olivine and pyroxenes (Nafziger and Muan, 1967) suggest a small positive deviation from ideality, and hence support the conclusion reached here.

#### ACKNOWLEDGMENTS

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